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HEAVY METAL POLLUTION IN SOIL-PLANT SYSTEM AND ITS REMEDIATION

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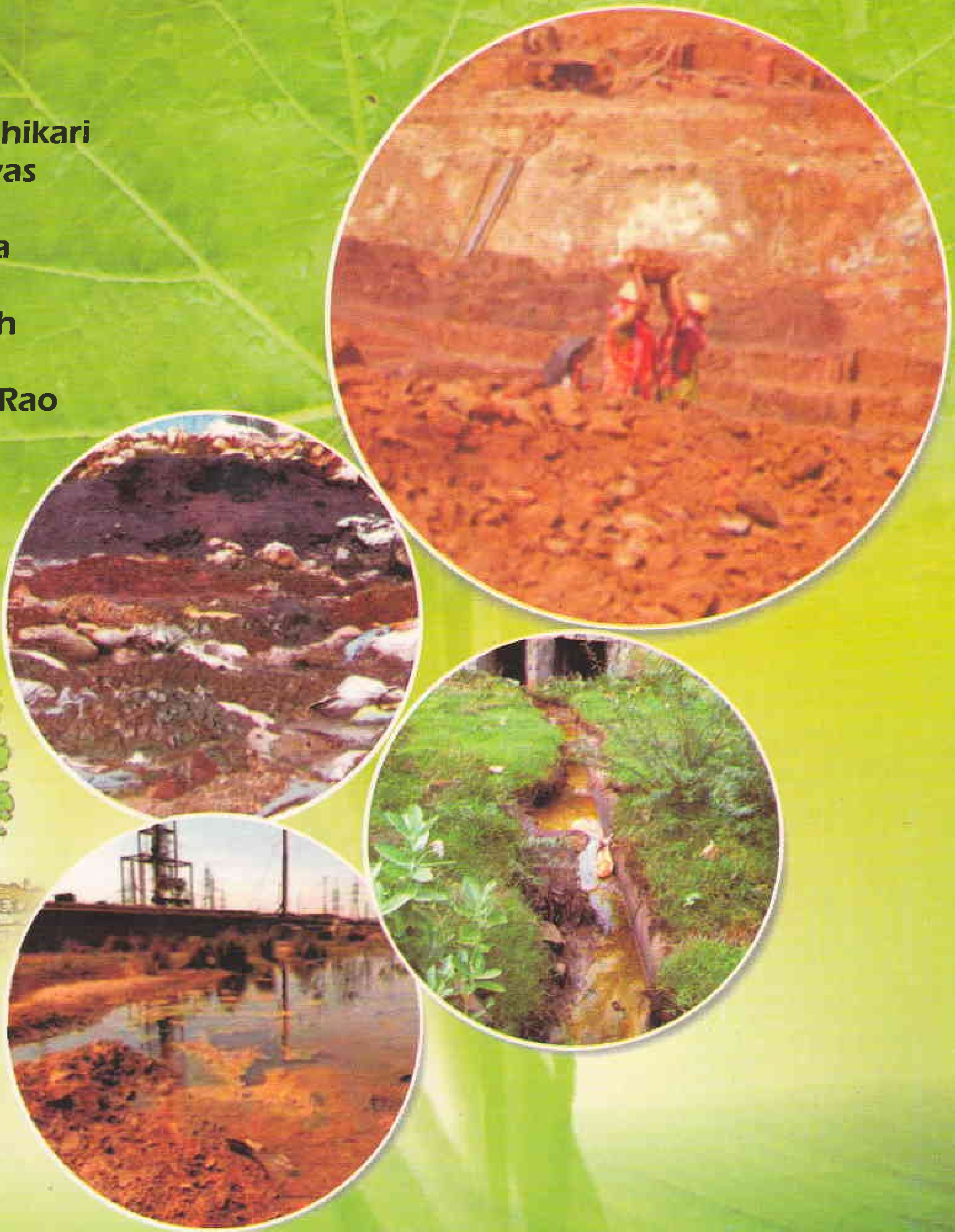

DIVISION OF ENVIRONMENTAL SOIL SCIENCE
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FOREWORD

The industrial development, rapid urbanization and population expansion experienced by many Indian cities during recent decades have resulted in a significant increase of heavy metal pollution, consequently, environmental contamination has become a major issue of serious concern. The heavy metals, which occur naturally in all soils and waters on absorption by living organisms in excessive concentrations, can have a severe toxic impact on living systems. We also need to recognize the fact that tge variation of chemical reactivity and mobility of each pollutant metal in different natural environments affects redistribution in soils, landscapes, the hydrological system, and passage through the food chain. These differences need to be recognized so that oversimplication can be avoided when assessing the ecological consequences of any polluting activity and for providing guidelines for safe agricultural practices. Dispersal of heavy metals and their largely irreversible retention by soils have long term consequences. Metals reaction with soils must be thoroughly understood to accurately assess their impact on the future problems of food quality and safety and plan necessary remedial measures. Currently, remediation of polluted areas and the reduction of health risks have received considerable attention from environmental scientists, including soil chemists, who have focused on the evaluation of organic and inorganic adsorbent materials for heavy metals immobilization in soils or their removal from contaminated water and soils. It is interesting to note that the authors have covered all the issues like survey, chemical process and remediation techniques of heavy metal pollution comprehensively in this technical bulletin. I congratulate the research team for their contributions and commendable efforts in disseminating the research results in the form of this bulletin. It is my belief and hope that this publication will serve as a useful reference material for researchers, developmental officials, extension personnel, policy makers and all those engaged in the activities related to soil health which ultimately impacts plant, human and animal health.

Date : January 10, 2012

Place : New Delhi

(A.K. Singh)
Deputy Director General (NRM), ICAR
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PREFACE

Indiscriminate disposal of waste, accidental and process spillage, mining and smelting of metalliferous ores, and sewage sludge application to agricultural soils are responsible for the migration of contaminants into non-contaminated sites contributing towards contaminants of our ecosystem. Major component of inorganic contaminants are heavy metals which present a different problem than organic contaminants. Generally heavy metals are toxic in high concentration because they can replace essential metals in pigments or enzymes disrupting their function. Consequently metals render the land unsuitable for plant growth and destroy the biodiversity. Due to lack of irrigation water the use of domestic and industrial effluents is unavoidable to irrigate the agricultural fields. The untreated effluents that emanate from the industry aggravate the accumulation of heavy metals in those soils. A trend of heavy metal accumulation in the agricultural fields surrounding Bhopal has been observed. The fate of metals in soils is dependent on various physical, mineralogical, chemical and biological processes that control their speciation, retention, solubility, transport and bioavailability. An understanding of sorption process and mechanism is crucial for the assessment of the heavy metals contamination and reclamation of such polluted soils. To express the adsorption process in a quantitative way, thermodynamic study is required to evaluate the free energy change corresponding to the transfer of cations and anions from the bulk solution into the appropriate parts of the double layer or lattice. The key areas on which investigations were carried out are survey, basic and fundamental chemistry and decontamination of polluted area to address the burning issue of heavy metal pollution comprehensively. Metal cations in the soil may exist in different chemical pools, and the equilibrium among these polls determines the bioavailability of these metals. We studied the mobility and fractionation of different heavy metals in different soils to assess the bioavailability. In this investigation a novel method was developed to calculate the sink capacity of soil. Metal contaminated soil can be remediated by chemical, physical and biological techniques as heavy metals cannot be chemically degraded and need to be physically removed or immobilized. The addition of various amendments to soils precipitates metals or increases metal sorption, thereby decreasing the concentration of the total metal ion in soil solution. Some of the amendments studied include lime, organic matter, compost, farm yard manure (FYM), vermicompost etc. to manage the heavy metal contaminated soils. Phytoremediation is an emerging technology and is considered for remediation of inorganically and organically contaminated sites because of its cost- effectiveness, aesthetic advantages, and long term applicability of some plants to accumulate high concentrations of heavy-metal ions. Phytoremediation research to date has been confined mainly to hyperaccumulating plants with an ability to concentrate high amounts of pollutant metals in their tissues. In this investigation we used different type of plants that may be cultivated from low to highly contaminated soils. Study on phytometallophore, a new concept used in phytoremediation, was also carried out to know the mechanism of plant accumulation of heavy metal.

We express our sincere thanks to our DDG (NRM), ICAR, Dr. A. K. Singh and Director, A. Subba Rao for their generous guidance, constructive suggestions and providing the facilities. We are grateful to all those who have given their valuable inputs from time to time in accomplishing this research work notably the scientific fraternity of Indian Institute of Soil Science, Bhopal. The immense help rendered by the technical and supporting staff of different divisions of IISS is gratefully acknowledged.

Authors hope that salient achievements of the project presented in this bulletin may be useful for research workers, progressive farmers, various extension agencies and policy makers.

Authors

Introduction

In recent years, contamination of large areas of land by heavy metals has become a major concern. It originates mainly from municipal waste disposal sites, incinerators, car exhausts, residues from metalliferrous mining and the smelting industry, and the use of urban compost, pesticides, fertilizers or sludge and sewage. The sewage is characterized by a complex heterogeneous multifaceted matrix depending upon its origin and production. Sewage generated in rural areas and small cities does not cause serious concern and fits well for recycling in agriculture due to its high contents of organic matter and major and micro nutrients. In contrary, urban sewage represents an admixture of sewage and industrial waste effluents which get contaminated with heavy metal pollutants. With increased industrialization in residential areas, different materials are discharged into sewage which lead to environmental pollution. Untreated sewage is applied for longer periods to grow crops on urban peripheral lands and it is a matter of great concern. Urban sewage containing industrial effluents was found to carry relatively high amounts of heavy metals such as Ni, Cr, Pb, Cd, Co and salt load causing salinity and alkalinity hazards (Clemente *et al.* 2003). Heavy metal pollution deteriorates the quality of soil and crops produced. Extent of soil pollution with heavy metals from various anthropogenic sources and subsequent uptake by crops depend upon several factors such as source, soil type, frequency of application, organic matter content, seasonal variations, major and minor nutrients and load of chemical pollutants. Continuous irrigation with untreated sewage, particularly in arid and semiarid regions of the developing countries, is often a potential source of heavy metal pollution to soil and plants and poses health risk to animals and humans. Excessive metal concentrations in contaminated soils can result in decreased soil microbial activity and soil fertility, and yield losses. Remediation of heavy metal contamination in soils is difficult. The conventional technologies for removing heavy metal from soils often employ stringent physicochemical agents, which can dramatically inhibit fertility and leaves subsequent negative impacts on the ecosystem. Numerous methods have been proposed to remove heavy metals form sewage sludge, including chlorination, use of chelating agents and acid treatments at high temperatures. However, those methods are generally ineffective in practical applications due to high cost, operational difficulties and low metal leaching efficiency. An alternative way to replace chemical methods in removing heavy metals is bioremediation through microbial leaching. Bioremediation is the process of cleaning up hazardous wastes with micro organisms or plants and is the safest method of clearing soil of pollutants. The chief concern of bioremediation research on soil contaminated with toxic chemicals is the removal of toxic substances so that neither soil nor water is harmful to animals, humans, plants or beneficial microbes. Bioremediation has been proposed as a cost effective, environment- friendly alternative modern emerging technology, which can be applied to a number of contaminants and site conditions. The current gap between understanding of bioremediation process and its application in field provides incentive to examine the use of microbes to reduce the heavy metal load from sewage water. Phytoremediation can be defined as the destruction, inactivation or immobilization of the pollutant in a harmless form primarily mediated by photosynthetic plants. The plants selected for phytoremediation must also be responsive to agricultural practices and produce sufficient biomass coupled with high rates of metal uptake. The plant must also be adapted to the wide variety of environmental conditions that exist in contaminated soils and waste sites. The application of phytoremediation in the field requires the integration of a variety of skills and techniques. The appropriate plant for the field conditions must be combined with agricultural techniques that support the application of soil amendments to enhance plant availability of the metal contaminants in order to achieve a successful remediation programme. The integration of specially selected metal accumulating crop plants with innovative soil amendments allows plants to achieve high biomass and metal accumulation rates from soil. Successful implementation of phytoremediation in the field depends on a significant quantity of metal being removed from the soil through plant uptake to effectively decrease the soil metal concentration. Chemical and phytoremediation have been proposed as cost effective, environmental friendly alternative technologies. Different chemical treatments brought about the changes in the speciation and extractability of heavy metals and their availability to plants. Suitable chemical treatments and screening of plants need to be developed for specific location.

2. Survey of contaminated areas

Survey of heavy metal polluted sites in India is of great significance as it help in gathering information and providing inventory of contaminated sites. The survey also helps in interpretation of data for use in agriculture (Pertsemli and Voutsa, 2007), forestry etc. and subsequently i predicting the adaptability of soils to various uses and also their behaviour and productivity unde defined set of management practices. Accumulation of heavy metals in crops grown in metal polluted soil may easily cause damage to human health through food chain. It is important t identify the sources and status of soil contamination by toxic metals so as to take proper treatment to reduce soil contamination and to sustain agricultural development. Most of the data related t polluted sites under the government projects are locked and not being published. Against th backdrop, a survey was conducted to monitor the influence of city sewage irrigation on the hea metal build up in soils around Bhopal. The area covered under this survey in surrounding Bhop viz. Jahangirabad, By-pass Road-I, By-Pass Road –II, Super Bazar, Mandideep, Islamnagar, Kol village and Ashok Nagar. Concentration of the metals in effluent was within safe limits (Table 1 2). Diethylene tri amine penta acetic acid (DTPA) extractable Pb, Cd, Ni, Co, Cr, Fe, Mn, Zn and C in the sewage irrigated surface soil ranged 3.5-6.8,0.15-0.40,2.56-5.58, 1.59-3.89, 0.45-0.55,3 15.8,3.6-8.5,1.2-3.6, 1.53-6.59 mg kg^{-1} respectively (Table 3) in those arrears. Continuous sewa irrigation resulted in accumulation of Pb, Cd, Ni, Co, Cr, Fe, Mn, Zn and Cu in surface 0-15 cm layer by 5,6, 0.4, 8, 0,6, 3.16,5,2,3 times more compared to adjoining tube well irrigated soils. Studies revealed that accumulation of heavy metals such as Pb, Cd, Ni, Co, Cr, Fe, Mn, Zn and Cu (Table 4) was higher mostly in the roots of various crops irrigated with city sewage effluent compared to that of tube well water irrigated crops. Amongst the crops, carrot and spinach showed the tendency of greater metal accumulation. Heavy metal contents of sewage samples recorded below the toxic levels, but continuous and indiscriminate use of sewage may cause toxicity in soils in future. Soils and plant samples collected from sewage irrigated fields showed the accumulation of heavy metals in soils, and vegetable crops recorded higher amounts than that of cereal crops.

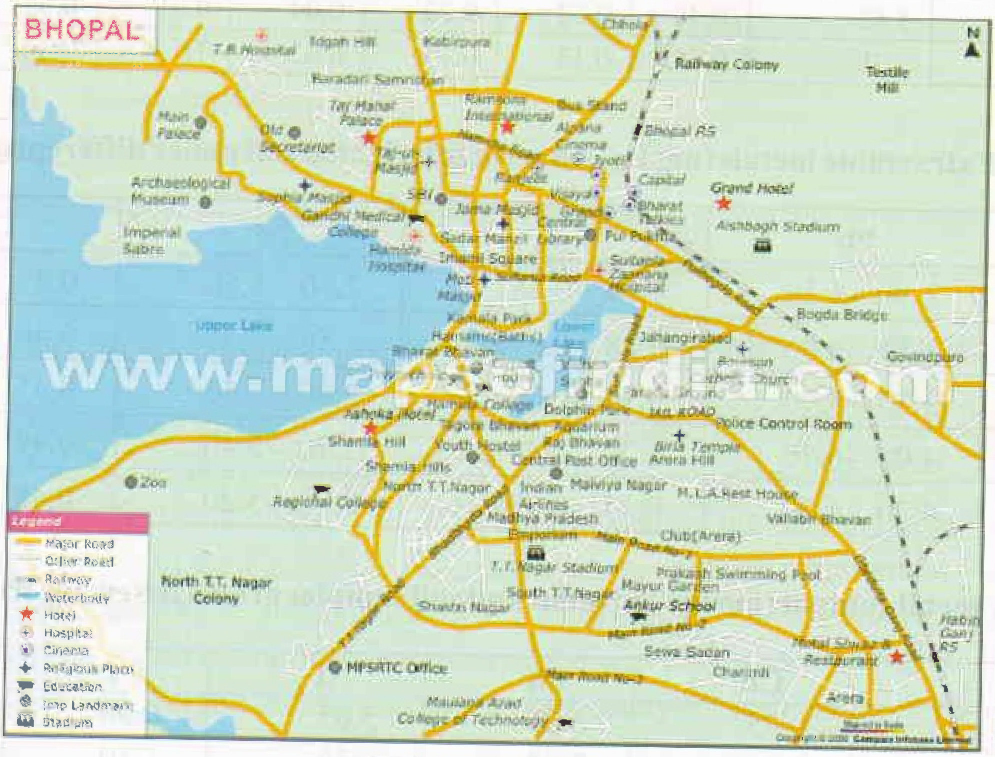


Table 1. Chemical characteristics of untreated city waste samples collected from different sites around Bhopal, M.P.

Location	pH(1:2.5 H_2O)	EC (dS/m)	Ca^{+2} (meq/L)	Mg^{+2} (meq/L)	CO_3^- (meq/L)	HCO_3^- (meq/L)	Cl^- (meq/L)
Tap water	7.2	0.29	3.9	2.30	-	1.6	1.00
Jahangirabad	8.1	1.19	4.2	4.2	-	2.4	3.81
By-Pass Road-I	7.9	0.98	3.87	5.13	-	3.2	3.31
By-Pass Road-II	7.9	0.59	4.30	4.10	-	2.4	1.80
BHEL	7.8	0.45	3.50	0.9	-	1.6	1.15
Ashok Nagar	7.6	1.00	3.20	8.6	0.8	2.4	1.94
Super Bazar	8.1	1.89	4.10	8.7	0.8	2.4	3.16

Table 2. Chemical characteristics of untreated city waste samples collected from differe sites around Bhopal, M.P.

Location	Fe	Mn	Zn	Cu	Co	Cr	Pb	Ni
	ppm							
Tap water	4.99	0.16	0.05	0.08	0.02	Tr	Tr	Tr
Jahangirabad	10.10	0.30	0.04	0.10	0.04	0.01	0.11	Tr
By-Pass Road -I	7.80	0.60	0.06	0.05	0.03	0.02	0.15	Tr
By-Pass Road -II	3.28	0.80	0.07	0.09	0.05	0.01	0.09	Tr
BHEL	8.09	0.39	0.15	0.18	0.08	0.03	0.22	0.15
Ashok Nagar	5.85	0.40	0.22	0.22	0.04	0.01	0.52	0.20
Super Bazar	9.39	0.65	0.13	0.13	0.02	Tr	0.44	0.24

Table 3. DTPA Extractable metals (mg kg^{-1}) in sewage irrigated soil under different areas

Crop	Pb	Cd	Ni	Cr
Radish	3.90 -6.30	0.19 -0.38	2.60 -5.50	0.47 -0.50
Onion	3.50 -6.80	0.18 -0.37	2.56 -5.58	0.46 -0.52
Wheat	3.70 -5.90	0.14 -0.39	2.60 -5.50	0.45 -0.55
Spinach	4.00 -6.70	0.20 -0.40	2.70 -5.40	0.49 -0.52
Carrot	4.20 -6.20	0.15 -0.42	2.70 -5.20	0.48 -0.50

Table 4. Heavy metal content (mg kg^{-1}) in plant and soil samples grown in sewage treated so

Plants	Cd	Pb	Ni	Cr	Cu
Wheat shoot	0.95	6.25	5.05	0.90	9.30
Wheat root	1.25	7.75	6.35	1.10	10.25
Carrot shoot	1.00	8.80	7.75	0.93	8.50
Carrot root	1.40	9.39	8.59	1.15	9.25
Onion shoot	0.98	6.40	6.30	0.94	9.30
Onion root	1.45	9.30	8.43	1.13	10.2
Radish shoot	1.00	5.55	9.05	0.91	7.35
Radish root	1.32	8.45	10.62	1.14	8.25
Spinach shoot	1.10	7.39	10.32	0.94	8.85
Spinach root	1.50	10.30	11.47	1.25	10.3

3. Fate of heavy metals in soil

The fate of metals in soils is dependent on various physical, mineralogical, chemical and biological processes that control their speciation, retention, solubility, transport and bioavailability. Some of these are

- i) Ion exchange
- ii) Specific adsorption
- iii) Surface precipitation
- iv) Dissolution/precipitation
- v) Chelation/complexatuion
- vi) Redox transformation
- vii) Uptake, fixation and transformation by plants and soil biota
- viii) Release from living (exudation) and dead biomass (decomposition)
- ix) Water transport within the soil profile and leaching.

4. Heavy metal reaction and transformation in major soil of India

Indiscriminate disposal of city wastes, sewage, industrial effluents and solid wastes aggravated the heavy metal pollution in soils and plants with cadmium (Cd), lead (Pb), chromium (Cr) (VI), and nickel (Ni), cobalt (Co) This has emphasized the need to improve our knowledge of the basic chemistry of these metals in soil-plant system. Sorption reactions on soil mineral surfaces potentially attenuate toxic soil solution (Poykio *et al.* 2002). An understanding of sorption process and mechanism is crucial for the assessment of the heavy metal contamination and reclamation of such polluted soils. Cd and Pb sorption vary among soil types and depend on various factors such as the chemical and mineralogical characteristics of the soils. Among these factors, the dependence of sorption on the amount of contaminant present in soil has often been studied in terms of different kinds of exchange isotherms to understand the sorption process involved and to determine sorption capacity of different soils (Arias *et al.* 2005). To gain further insight into sorption process and its mechanism, thermodynamic approach can be employed to predict the final state of metal in the soil system from an initial non-equilibrium state (Adhikari and Rattan, 2002). Evaluation of the free energy change corresponding to the transfer of element from bulk solution into the appropriate site of the double layer or clay mineral lattice is helpful to express the sorption process. Similarly, an understanding of change in enthalpy and entropy helps in determining the free energy change and disorders occurring during sorption process. Such information on heavy metal sorption is lacking for Indian soils. Sorption parameters of different heavy metals are discussed below:

4.1 Cadmium sorption

Cadmium is considered as one of the important soil and environmental pollutants, as it is th most potential biotoxic heavy metal that is readily absorbed by plants and gets entered into th animal and human food chain. The greatest concern due to cadmium contamination is because of i occurrence in free ionic form. The various possible sources of cadmium contamination i agricultural soils are through land disposal of sewage and sludges, industrial wastes and effluen and from application of phosphatic fertilizers containing Cd as impurities. Sorption of Cd mainl involves the free divalent cation Cd^{+2} (Apple and Ma, 2002). So, knowledge of Cd sorption in soil i important in order to know its persistence and transport in soil . Concentration of heavy metals i soil solution and their bio-availability are controlled by sorption reactions at soil colloids, which a influenced by soil properties. A study was undertaken to compare the Cd sorption characteristics o Vertic Ustochrept, Typic Eutrochrpt, Typic Ustochrept. Typic Ustipsamment, Typic haplustalf a Typic Ustothrent representing five agro-ecological regions of India. Sorption of Cd could b predicted satisfactorily by Freundlich equation and modified Langmuir equation (Adhikari a Singh, 2000). These could predict sorption of Cd at lower concentration up to 5 mg L^{-1} o equilibrium solution. Vertic Ustochrepts and Eutrochrept soils showed maximum Cd sorpti capacity and the lowest by Ustipsamment. Such differences in Cd sorption capacity were related t differences in soil physicochemical properties. Sorption maxima (b) and the Freundlich consta (K_f) of cadmium were positively correlated to cation exchange capacity (CEC), clay, Ca CO_3 and p (Adhikari and Singh, 2005).

A study was also undertaken to know the Cd adsorption behaviour in four major soil grou suborders of Indo Gangetic alluvial plains (IGP) viz. sandy loam (Typic Ustochrept) of Ludhian sandy loam (Typic Ustipsamment) of Hisar representing Trans IGP zone, sandy clay loam (Ty Ustochrept) of Morena and sandy loam (Typic Eutrochrept) of Varanasi of Central IGP zone a clayey (Typic Endoaquept) of Midnapur of Eastern lower IGP plains. Studies showed t adsorption of Cd can be satisfactority predicted by conventional Langiuir and Freundlich equatio but split Langmuir isotherm gave better prediction by 13-15 per cent over conventional Langm isotherm. Cadmium adsorption capacity was the lowest in sandy loam Typic Ustochrept follow by Ustipsamment, Eutrochrept but was the highest for clay loam Endoaquept soil. Such differen in Cd sorption capacity were related to differences in soil physico-chemical properties, mai cation exchange capacity (CEC), clay and pH irrespective of soil sub group/orders.It was obser that higher Cd adsorption capacity occurred in sandy clay loam than sandy within same Ty Ustochrept suborder. The study indicated that the occurrence of Cd toxicity would be in the orde clayey > sandy loam> sandy clay loam> sandy loamy representing Endoaquept, Eutrochr Ustochrept and Ustipsamment sub orders. Thus coarse textured soils of Trans – IGP zone, wh are also consuming maximum phosphatic fertilizers about two times compared to eastern zone, would be more vulnerable to Cd toxicity; therefore, strategies to reduce the Cd contamination in soil environment need a fresh look considering Cd adsorption properties of soils and Cd load in fertilizers and /or sewage –sludge (Singh and Adhikari, 2001).

4.2 Lead sorption

In recent years, Pb contamination in soils is a major problem throughout the world. Sources of Pb contamination in soils may be resulted from industrial activities such as mining and smelting processes, agricultural activities such as application of insecticide and municipal sewage sludges and urban activities such as use of Pb in gasoline, paints and other materials. Lead has been acknowledged to be the most abundant metal pollutant in the environment and can cause toxicity in humans (Yang *et al.* 2004). The level of lead in the environment has increased significantly as a result of industrialization and urbanization. Since the half-life of lead in biological systems is one of the longest among metals, the consequence of lead pollution can be far-reaching and devastating. Lead occurs in soils in the form of insoluble and soluble salts. It tightly binds to organic soil particles, which may decrease the mobility of lead in most soils and may reduce uptake by plants. To evaluate the sorption mechanism of lead (Pb) in major soil types, an experiment was conducted on different soils representing five agroecological zones (AEZ) of India. The thermodynamic parameters viz. K°, G°, H° and S° were determined by using sorption concentrations of Pb in equilibrium solution at two different temperatures 25 °C ± 2 and 45° C ± 2 of soil suspension. Results showed that the data of heavy metals sorption could be described satisfactorily by Freundlich and modified (two surfaces) Langmuir isotherms. The Pb sorption was in the order of in the Vertic Ustorthent>Typic Eutrochrept>Typic Ustochrept> Typic Haplustaff>Typic Ustorthent. The Vertic Ustochrept sorbed Pb 2.0 and 1.9 times more than that of Ustorthent and Haplustalf soils, respectively. Such variations in Pb sorption maxima were correlated with the differences in pH, CEC and organic matter content of the soils.

4.3 Nickel sorption

The contamination of agricultural lands caused by nickel in and around industrial areas is a serious problem. Nickel is not considered to be an essential nutrient for higher plants. But nickel has also been reported to stimulate growth at low concentrations, while producing toxic effects at high concentrations. Since Ni is ubiquitous in the environment, it is a normal constituent of plant tissue. Nickel is usually absorbed in the ionic form Ni^{+2} from soil or culture media and has been reported as a stable species over a wide range of pH and redox conditions. A number of soil factors such as CEC, pH, texture, $CaCO_3$ content, organic matter, sesquioxides, and chelating agents have been reported to influence Ni sorption. Once Ni enters the soil, it interacts with its organic and inorganic constituents thereby undergoing transformation into various forms like soluble, exchangeable, bound to carbonate, Fe –Mn oxides, organic matter and residual and subsequently its bio-availability varies. Studies were conducted to characterize adsorption of nickel (Ni) in soils and its thermodynamic parameters (K°, ΔH°, ΔS°, ΔG°) by equilibrating the soil samples with graded levels of Ni at 25° C± 2 and 45° C± 2 (Adhikari and Singh, 2005). The soils were classified as Vertic Ustochrept, Typic Eutrochrept, Typic Ustipsamment, Typic Haplustalf and Typic Ustorthent representing five major agro-ecological zones of India. The adsorption data of Ni could be described satisfactorily by both Freundlich isotherm equation and conventional Langmuir equation. Amongst soil types, Vertic Ustochrept clay soil showed maximum adsorption maxima for Ni followed by Eutrochrept > Ustipsamment > Haplustalf > Ustorthent soil. The adsorption maxima for Ni in Vertic Ustochrept soil was 1.51 and 1.40 times more than these in Ustorthent and Haplustalf soils.

4.4 Chromium sorption

Chromium is unique amongst the heavy metals found in industrial waste water and sewage and sludge, in that it may exist as a trivalent cation and as an ion in the hexavalent state in the pH range of agricultural soils. Chromium (VI) is the most mobile, reactive, and toxic chromium form and it would be the only existing form if all chromium were to be in thermodynamic equilibrium with the atmosphere. Wastes from the metallurgic, refractory, chemical, and tannery industries contain variable amounts of Cr (III), mainly as $Cr(OH)_3$, or as complexes with organic compounds. Incorporation of such materials into soils could result in potentially dangerous pollution of ground water if the Cr is oxidized in quantity to the soluble chromate anion. The hexavalent form of Cr (CrO_4^{-2}) being the most active in soils is of particular concern because this form has been demonstrated to be toxic at low concentrations to both plants and animals. The hexavalent chromium is a strong oxidizer and as a result exists only in oxygenated species that are soluble and pH dependent and occurs as an anion in aqueous solution.

To study the sorption of chromium in major soil types, an experiment was conducted on Typic Ustorthent, Typic Haplustalf, Typic Eutrochrept, Vertic Ustopept, Sodic Haplustert representing five agroecological zones of India. Results showed that the data of Cr sorption could be described satisfactorily by Freundlich and modified Langmuir isotherms. The order of Cr sorption was in the order; Typic Ustorthent > Typic Haplustalf > Typic Eutrochrept > Vertic Ustopept > Sodic Haplustert. The Typic Ustorthent sorbed Cr 1.5 and 2.0 times more than their sorption by Vertic Ustopept and Sodic Haplustert soils, respectively (Adhikari and Singh, 2003). Such variations in Cr sorption maxima were correlated with the differences in pH, CEC and organic matter content of the soils. A laboratory experiment was conducted to study the thermodynamics of chromium sorption in major soil types, viz Typic Ustorthent, Typic Haplustelf, Typic Eutrochrept, Vertic Ustopept, Sodic Haplustert, representing 5 agroecological zones of India. The thermodynamic parameters, viz. thermodynamic equilibrium constant (K°), standard free energy (G°), standard enthalphy (H°) and standard entropy (S°) were determined.

By using sorption data and concentrations of Cr(VI) in equilibrium solution at temperatures 25 °C ± 2 and 45° C ± 2 of soil suspension. Data of Cr sorption could be described satisfactorily by Freundlich and modified Langmuir isotherms. The Cr sorption was maximum in order of Typic Ustorthent >Typic Haplustalf> Typic Eutrochrept > Sodic Haplustert. The Typic Ustorthent sorbed Cr 1.5 and 2.0 times more than the sorption by Vertic Ustopept and Sodic Haplustert soils respectively. Such variations in Cr sorption maxima were correlated with the differences in pH, cation-exchange capacity (CEC) and organic matter content of the soils (Adhikari and Singh, 2007).

4.4.1 Chromium (VI) sorption with different heavy metals in Inceptisols

Generally, the retention of Cr (VI) in soils having high pH (pH > 7.0) is negligible because of the soil's negative surface charge, which aggravates the negative sorption of Cr (VI) by negative leaching phenomenon. However, the presence of different heavy metal cations may increase the sorption of Cr (VI) in these soils. So for better understanding of mechanisms responsible for differential sorption of Cr (VI) in soil, laboratory experiments were conducted. This study evaluated the effect of different heavy metals viz. Pb, Cd, Ni and Zn on Cr (VI) sorption in Inceptisols. Kinetics study revealed that cation sorption was more rapid and took place during the first hour; where as sorption of Cr (VI) was slower. The presence of heavy metal cations in the solution matrix increased the sorption of Cr (VI) by the Inceptisols, but Cr (VI) sorption was negligible, in the range of 0 - 0.03 mM in the absence of heavy metal cations. In the presence of cations, sorption of Cr (VI) was first observed at an equilibrium concentration of 0.008 mM for the Delhi, Typic Ustochrept, soil and 0.02 mM for the Hisar, Typic Ustochrept, soil (Adhikari, 2010). Based on the calculated distribution coefficient (Kd) for those metals, Pb generally exhibited the highest affinity for soil sorption. Investigation was also conducted to determine the individual effect of heavy metals on Cr (VI) sorption, and it was found that amongst the studied heavy metal cations Pb strongly influenced the sorption of Cr (VI) in soil.

4.5 Cobalt sorption

The discharge of cobalt in soil and its accumulation by plant and organisms drawing attention to the cycling and fate of this element in soil environment. Cobalt, an essential element that plays a very specific role in vitamin B12 synthesis. The sorption and desorption characteristics of cobalt in soil and/or groundwater systems are very important with respect to environmental pollution, and these processes are influenced by several factors. Considering Co as potential hazard, ground wa contaminant and its phytotoxicity, it is necessary to understand the influence of soil properties adsorption of cobalt and its thermodynamic parameters in soils.

Studies were conducted to characterize adsorption of Co in soils and its thermodyna parameters (K°, ΔH°, ΔS°, ΔG°) by equilibrating the soil samples with graded levels of Co at 2 2°C and 45± 2°C (Adhikari and Singh, 2005). The soils were classified as Vertic Ustochrept, Ty Eutrochrept, Typic Ustipsamment, Typic Haplustalf and Typic Ustorthent representing five ma agro-ecological zones of India. The adsorption data of Co could be described satisfactorily by b Freundlich isotherm equation and conventional Langmuir equation. Amongst the soil types, Ver Ustochrept clay soil showed maximum adsorption maxima for Co followed by Eutrochrep Ustipsamment > Haplustalf > Ustorthent soil. The adsorption maxima for Co in Vertic Ustochr soil was 3.73 and 1.42 times more than that Ustorthent and Haplustalf soil.

4.6 Competitive sorption behaviour of Pb and Cd

The competitive sorption behaviour of cadmium (Cd) and lead (Pb) was assessed from t single or mixed solution matrix in surface soil samples of three soils, namely, Jabalpur (Vertis Patancheru (Alfisol) and Barrackpore (Inceptisol), having diverse physicochemical properti Sorption isotherms of Cd and Pb in all three soils have been prepared and sorption data have be fitted into different isotherm equations to get best fit. By and large Langmuir equation be described the sorption of Cd and Pb in all three soils. Soils with higher pH and clay content had t greatest sorption capacity as estimated by the maximum sorption parameter of the Langm equation. In general, Pb sorption was greater than Cd sorption in all the soils and because of t competitive sorption of Cd and Pb for the same sites, Cd sorption was lower in presence of Pb in t solution matrix. Based on the fitness of sorption data, various sorption parameters have also be calculated (Adhikari and Singh, 2003). The results demonstrate a significant interaction betw Pb and Cd sorption when both metals are present that depends on important soil properti Competitive Cd and Pb sorption in Kheri soil was studied from a mixed solution matrix, wher 100 mg L^{-1} Cd and Pb was added in different proportions in such a way that at one end it was 100 m L^{-1} Cd and at the other end 100 mg L^{-1} Pb only (Fig. 1). Cd sorption curve could be explained w two distinct straight lines having distinctly different slopes. In presence of higher proportion of P in the solution matrix, Cd sorption curve maintained a lower slope than when the proportion of C was higher in the solution matrix. That explained the fact that in presence of Pb, the sorpt capacity of Cd was suppressed. However, there was no effect of Cd on Pb sorption and, theref the Pb sorption curve had by and large the same slope. The total Cd+Pb sorption declined slightl presence of higher proportion of Cd in the equilibrium solution due to lower sorption capacity of t soil for Cd as compared to Pb.

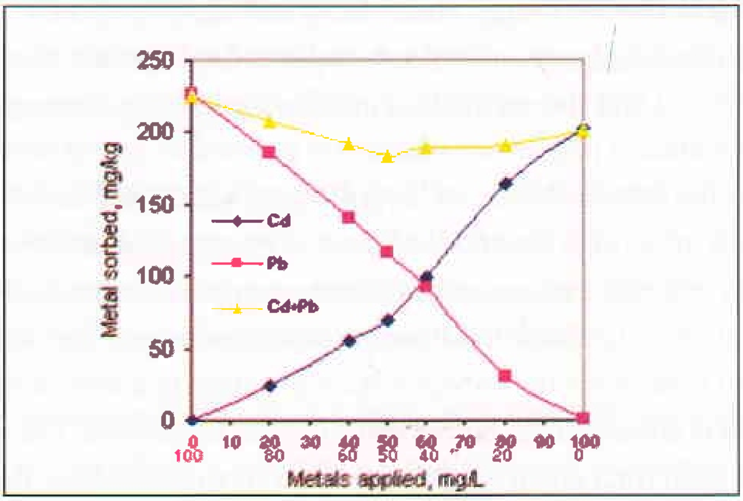


Figure1. Competitive sorption behaviour of Pb and Cd in soil

5. Thermodynamic study of heavy metal sorption in soils

Thermodynamics is the science of energy conversion involving heat and other forms of energy, most notably mechanical work. It studies and interrelates the macroscopic variables, such as temperature, volume and pressure, which describe physical and thermodynamic systems. Thermodynamics describe how systems change when they interact with one another or with their surroundings. This can be applied to a wide variety of topics. To express the adsorption process in a quantitative way, evaluation of free energy change corresponding to the transfer of cations and anions from the bulk solution into the appropriate parts of the double layer or lattice. It is important to understand how the properties of the individual ions influence the driving force of the net adsorption process. Unfortunately the necessity of preserving electrical neutrality makes it impossible to study a process in which only the cation or only the anion is adsorbed. Thus there is an inherent difficulty in deciding how much each kind of ion contributes to the net value of driving force. This difficulty can be largely avoided when one can assume that the counter ion is non-specifically adsorbed. For any process the free energy change is:

$$F = (ni\ f_i)\text{products} - (ni\ f_i)\text{reactants}$$

Where ni= number of moles and $fi = f^{\circ}_i + RT \ln a_i$ is the partial molal free energy of component i.

If the temperature coefficient of F° is determined one can evaluate the standard entropy of adsorption, S° and the standard heat of adsorption, H° through the well known relations:

$$-S^{\circ} = [(F^{\circ})/T]_p$$

$$H^{\circ} = F^{\circ} + TS^{\circ}$$

Thus, by measuring at various temperatures the concentration of only the cation in a solu equilibrated with the two solid phases, adsorbent and standard surface complex, it is possib evaluate both the geometrical and the energetic contributions to the driving force of the stan adsorption process. This standard process or reaction is defined as one in which a mole of catio the bulk solution starts in its standard state of 'hypothetical ideal one mole' (unit activity), re with the surface of a given mineral in its standard state. The standard adsorbed state is defined distinct phase existing as a surface complex of definite composition and unknown thickness corresponding to some arbitrarily fixed fractional surface coverage. The standard free energ adsorption is a measure of how much the concentration of cation in solution must diminish, star with activity of the cation is equal to one, before equilibrium is reached. The greater the adsor of the cation in a given system for a given equilibrium cation concentration, the more negative value of the standard free energy. At constant pressure, and with no non-mechanical work b done by the system, H° is the heat of adsorption of the standard adsorption process.

Because of the hydrated nature of the cation, it is thought that the removal or partial rem of the hydrated shell during adsorption functions as the major consumer of the energy th adsorbed in the system. In the endothermic systems, the H° values also serve as a measure o minimum activation energy governing the rate of adsorption as a function of temperature. change in entropy of a system S, is sensitive to any structural changes that may occur in a syste can be regarded as a measure of the order or disorder produced in a system during a given reac Intitutively, one would expect that the adsorption of ions from solution would produce more in a given system since the random motion of the ionic species in solution has become subjec the restraining adsorption force of the surface; i.e. the entropy change would be expected to h negative value. However, the hydrated nature of the adsorbed ion must also be considered in to obtain a complete picture of the entropy change. A hydrated ion that is strongly adsorbed is l to be at least partially dehydrated upon entering the adsorbed ionic layer. During the proce dehydration, the water molecules which were originally oriented about the hydrated io liberated and their return to the solution phase tends to increase the disorder of the system. Whe metal forms inner sphere complex in the system, sorption reaction indicates the endothe reaction (Figure 2).

5.1 Thermodynamic parameters of cadmium, lead, nickel, chromium and cobalt in soi

Thermodynamic parameters were derived (K°, ΔH°, ΔS°, ΔG°) by equilibrating th samples with graded levels of cadmium at 25° C ± 2 and 45° C ± 2 from a single solution matri high value of G° for Cd indicated that the reaction was spontaneous. The value of H°, whic negative for Cd, concluded that Cd sorption reactions were exothermic in all the soils. exothermic nature of Cd sorption may be attributed to the formation of different type of hy species of the metal ions and formation of the outer sphere complex with soil colloids via surface coordination (Figure 3). So the soils of tropical countries like India would be more vulnerable to Cd toxicity due to higher release of metals with increase in temperature.

Thermodynamic parameters revealed that heavy metal sorption increased as the value of K° G°, H° and S° increased with the temperature. The high values of G° for Pb indicated that the reaction was spontaneous. The value of H° was found to be positive for Pb concluded that Pb sorption sorption was found to be an endothermic reaction in all the soils.

Thermodynamic parameters viz. K°, ΔG°, ΔH° and ΔS° were also calculated to know the sorption reaction of Ni, which indicated that the reaction is endothermic and spontaneous in nature. The high values of G° for Cr indicated that the reaction was spontaneous. The value of H° was found negative for Cr indicating that Cr sorption reaction exothermic in all the soils.

Thermodynamic parameters viz. K°, ΔG°, ΔH° and ΔS° were calculated to know the sorption reaction of Co which indicated that the reaction is endothermic and spontaneous in nature.

Table 5.Thermodynamic reaction of heavy metal in soils

Sl. No.	Element	Thermodynamic Reaction	Possible Explanation
1	Cd	Exothermic	Outer Sphere Complex
2	Pb	Endothermic	Inner Sphere Complex
3	Ni	Endothermic	Inner Sphere Complex
4	Cr	Exothermic	Outer Sphere Complex
5	Co	Endothermic	Inner Sphere Complex

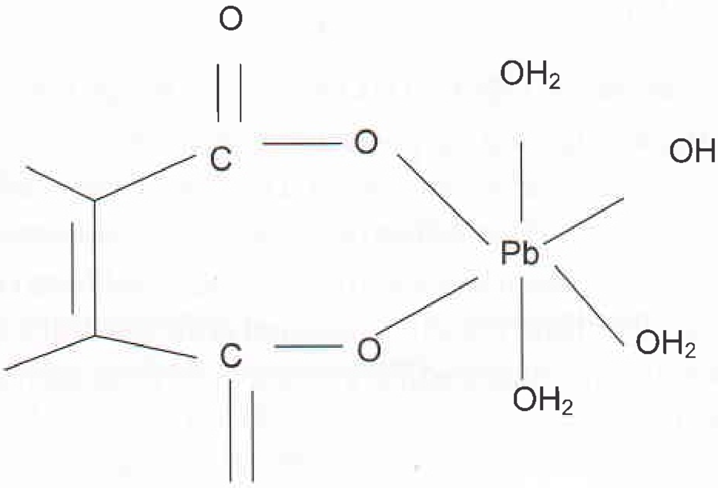


Figure 2. Inner Sphere Complex

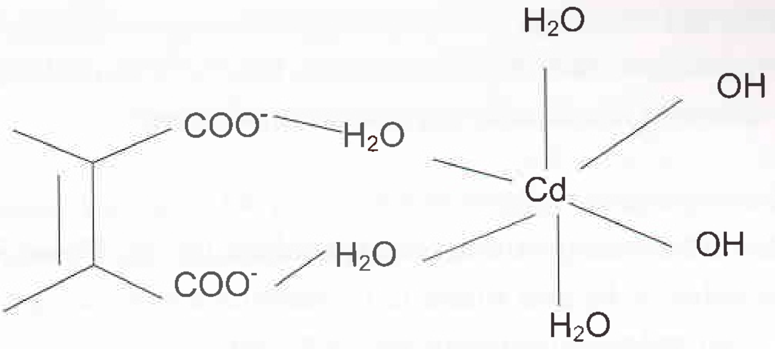


Figure 3. Outer Sphere Complex

Hence, by defining a standard adsorption process and then finding how the standard free energy of adsorption varies with temperature, thermodynamic data allow not only an exact and meaningful comparison of adsorptive capacities, but also permit some insight into the mechanism of cation adsorption. Thermodynamic study of heavy metal in soil revealed that in soils of tropical country like India would be more vulnerable to cadmium and chromium toxicity due to higher release of metal with increase in temperature.

6. Interaction effect of Cd and Pb on growth of spinach plant

The interaction effect of Cd and Pb on growth and metal uptake of spinach crop in a swell-shrink clayey soil of Jabalpur showed that in presence of Pb, both the plant Cd concentration and total Cd uptake by the spinach increased. But the Pb concentration in plant did not increase with the Cd treatments. Both the Pb (125 mg/kg soil) and Cd (25 mg/kg soil) reduced the vegetative growth of the spinach shoots, and a positive interaction of the two metals on growth was observed. An analysis of the underlying mechanism led to the conclusion that the effect of the added Pb was to increase the toxicity of added Cd.

The cumulative and interactive effects of six levels of Cd (0,2,4, 6,8 and 10 mg kg^{-1}) and six levels of Pb (0,20,40,80,100 and 125 mg kg^{-1}) on spinach were studied in a pot experiment. Dry matter yields of spinach at 25 and 45 days after sowing (DAS) are given in table 6 and 7. At both 25 and 45 DAS the interaction effect of Cd and Pb on dry matter yield of spinach was not significant. At 25 DAS, dry matter yields of spinach was significantly decreased from control at 6 mg Cd kg^{-1} soil level onwards, whereas significant reduction occurred at all levels of Cd addition at 45 DAS. However, in case of Pb, significant reduction in dry matter yield of spinach took place only at 100 mg kg^{-1} soil level onwards at both sampling.

Table 6. Dry matter yield (g pot^{-1}) of spinach at 25 DAS

Cd levels (mg kg^{-1})	Pb levels (mg kg^{-1})						
	0	20	40	80	100	125	Mean
0	4.90	4.92	4.94	4.82	3.75	2.58	4.32
2	4.81	4.83	4.85	4.71	3.62	2.48	4.22
4	4.75	4.73	4.70	4.65	3.51	2.33	4.11
6	4.62	4.64	4.66	4.51	3.40	2.20	4.01
8	4.40	4.42	4.44	4.30	3.21	2.02	3.80
10	4.11	4.12	4.14	3.96	3.05	1.87	3.54
Mean	4.60	4.61	4.62	4.49	3.42	2.25	
CD (P=0.05)			*Cd = 0.29, Pb = 0.35, CdXPb = NS*				

Table 7. Dry matter yield (g pot^{-1}) of spinach at 45 DAS

Cd levels (mg kg^{-1})	Pb levels (mg kg^{-1})						
	0	20	40	80	100	125	Mean
0	9.17	9.18	9.22	9.14	8.05	6.85	8.60
2	8.63	8.64	8.67	8.53	7.60	6.50	8.10
4	8.25	8.26	8.28	8.14	7.20	6.12	7.71
6	8.10	8.11	8.13	8.00	7.05	5.95	7.56
8	7.95	7.97	8.00	7.85	6.90	5.79	7.41
10	7.45	7.47	7.48	7.32	6.35	5.25	6.89
Mean	8.26	8.27	8.30	8.16	7.19	6.08	
CD (P=0.05)			*Cd = 0.22, Pb = 0.34, CdXPb = NS*				

7. Sink capacity of soils for toxic metal pollutants

Recycling wastes in agriculture is becoming an essential disposal method, and according to waste characteristics can produce supplementary organic matter resources (sewage sludge, compost) for crop production, or valuable soil amendments (coal fly-ash). Many waste products generally contain greater quantities of heavy metals than soil and in agronomic use there is the possibility that these elements could accumulate in the arable layer. The risk of the possible pollution of crops by heavy metals makes it necessary to use guidelines for waste utilization. Measurement of sink capacity of soils of different mineralogy is the most important prerequisite for making such guidelines.

7.1. Measurement of Short-term Sorption Parameters

Ten soils were characterized for their sorption behaviour of Cd and Pb from the single or mixed solution matrix in an effort to measure the sink capacity of these soils for Cd and Pb. Sorption isotherms of Cd and Pb in Kheri, Patancheru and Barrackpore soils have been prepared (Fig. 4). Vertisol (Kheri) sorbed the highest amount of Cd and Pb followed by Incptisol (Barrackpore) and Alfisol (Patancheru). Sorption of Cd and Pb was well correlated with the clay, organic matter and CEC of the soils. In general, Pb sorption was higher than Cd sorption in all the soils and because of the competitive sorption of Cd and Pb for the same sites, Cd sorption was lower in presence of Pb in the solution matrix (Fig. 5). Cd had no effect on the extent of Pb sorption by the soils.

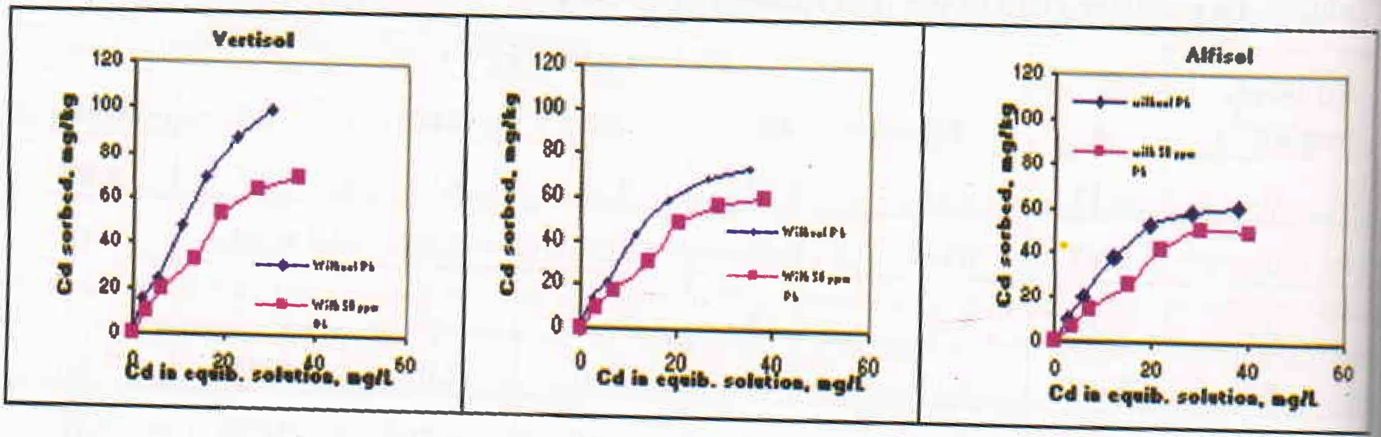


Fig.4 Cadmium sorption isotherms in mineralogically variant soils

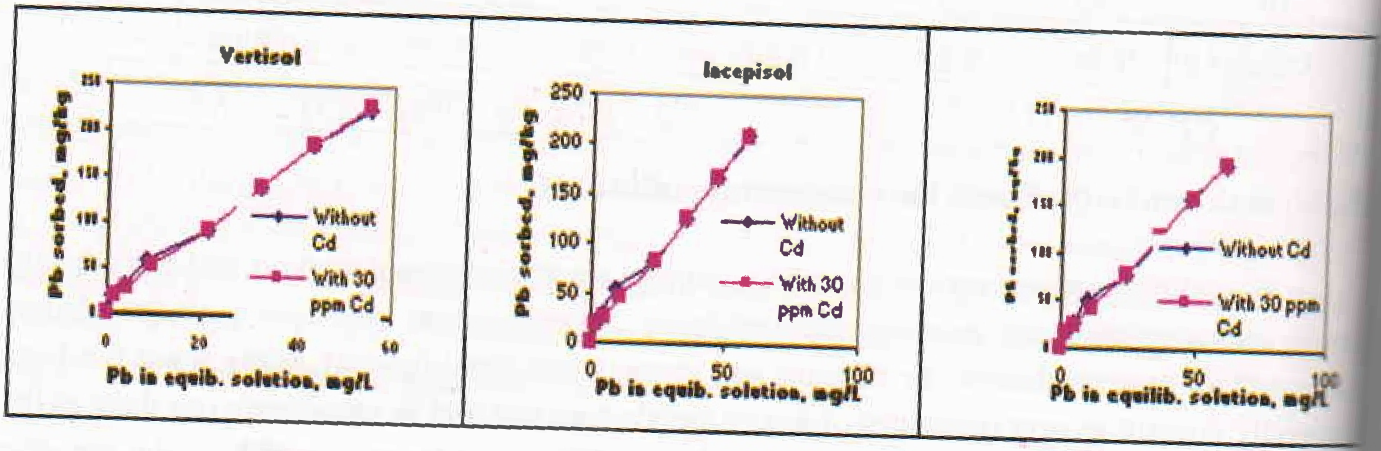


Fig.5 Lead sorption isotherms in mineralogically variant soils

Seven benchmark soil series, namely, Linga, Kagwad, Sarol, Bajatta, Lohara, Shahzadpur and Guttapalli having variant mineralogy were also used for Cd and Pb sorption study. Sorption isotherms of Cd and Pb in all seven soils have been prepared in a single solution matrix and sorption data have been fitted into different isotherm equations to get the best fit. By and large Freundlich and modified Langmuir isotherm equation best described the sorption of Cd and Pb in all seven soils. Based on the fitness of sorption data, various sorption parameters have also been calculated (Tables 3 & 4). The Freundlich 'k' values are indicative of the sorption capacity of different soils since 'n' values were at the same level (Maftoun *et al.* 2004) and on that basis Linga had the highest sorption capacity for Cd and Pb, and Guttapalli the lowest. The Langmuir 'b' values also maintained the same trend (Table 8 & 9).

Table 8. Cd sorption parameters for different soils

***Soil series* (Sub order)**	**Freundlich**		**Modified Langmuir**			
	K	**n**	**b I**	**k I**	**b II**	**k II**
Linga	7.18	5.35	36.27	4.40	943.4	0.007
Kagwad	7.12	5.48	33.68	4.30	840.3	0.006
Sarol	7.11	5.63	32.26	3.87	632.0	0.005
Bajata	6.54	5.52	30.25	3.18	600.0	0.004
Lohara	6.34	5.54	29.94	1.69	585.7	0.004
Shazadpur	5.46	5.34	29.41	0.75	530.2	0.003
Guttapalli	5.01	5.30	38.57	0.56	490.2	0.003

Table 9. Pb sorption parameters for different soils

Soil series (Sub order)	**Freundlich**		**Modified Langmuir**			
	K	**n**	**bI**	**kI**	**bII**	**kII**
Linga	7.23	5.21	41.98	3.00	1298.7	0.007
Kagwad	7.15	5.25	40.01	3.66	1162.4	0.006
Sarol	7.13	5.11	39.65	2.39	887.4	0.010
Bajata	6.98	5.20	38.87	1.99	854.7	0.009
Lohara	6.60	5.09	36.20	1.34	806.4	0.005
Shazadpur	5.98	5.05	32.44	0.61	758.2	0.005
Guttapalli	5.45	4.90	29.98	0.51	746.3	0.004

The correlation matrix between soil parameters and Cd and Pb sorption parameters clearly indicated that sorption of Cd and Pb by soils was highly dependent on soil pH, organic C, clay, CEC and free $CaCO_3$.

7.2. Sink Capacity of Soils Based on Chemical Soil Tests

Sink capacities of seven benchmark soil series, namely, Linga, Sarol, Bajatta, Lohara, were determined from the pure metal solution matrix based on chemical soil test method. Based on the single-surface Langmuir sorption maxima, the soil was incubated with different doses of a heavy metal. The treated soil was used for sequential extraction with either AB-DTPA or 4M HNO_3 to get the maximum or minimum non-recoverable amount, which was plotted against the amount of metal added (Fig. 6,7,8). The plateau values were considered as minimum or maximum sink capacity of the soil for the metal element in question depending on the extracting solution. Sink capacities of these seven soils have been determined from the pure metal solution matrix based on chemical soil test method.

Figure 7 and 8 depict the non-recoverable Cd and Pb, respectively, at different levels of metal contamination in soils. The plateau values of these figures were used to calculate the maximum and minimum sink capacity of these soils. Invariably, the maximum sink capacity of the soil was lower than the single surface Langmuir maxima (b_1), and the maximum (S_{max}) and minimum sink capacity (S_{min}) values followed the same trend as that of b_1 values (Table 8). In respect of both sorption capacity and sink capacity, the soils followed the order: Linga > Sarol > Bajatta > Lohara

Table 10. Single-surface Langmuir sorption maxima based sink capacities for different soils

Soil Series (sub-order)	Cadmium			Lead		
	b1	Smin	Smax	b1	Smin	Smax
Linga *(Udic Haplustert)*	36.3	26	30	42.0	32	36
Sarol *(Typic Haplustert)*	32.3	20	25	39.6	27	31
Bajatta *(Vertic Ustochrept)*	30.2	18	22	38.4	25	28
Lohara *(Typic Ustorthent)*	29.9	16	20	36.2	23	26

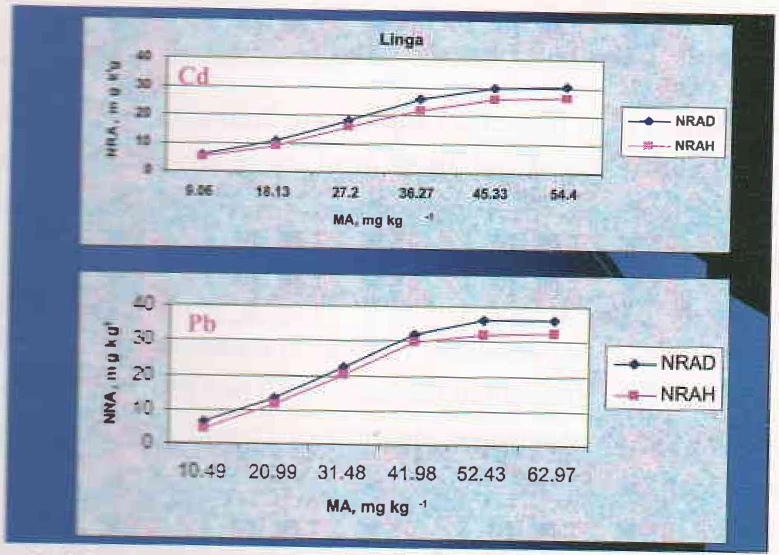


Fig. 6. Measuring sink capacity of a soil by chemical means

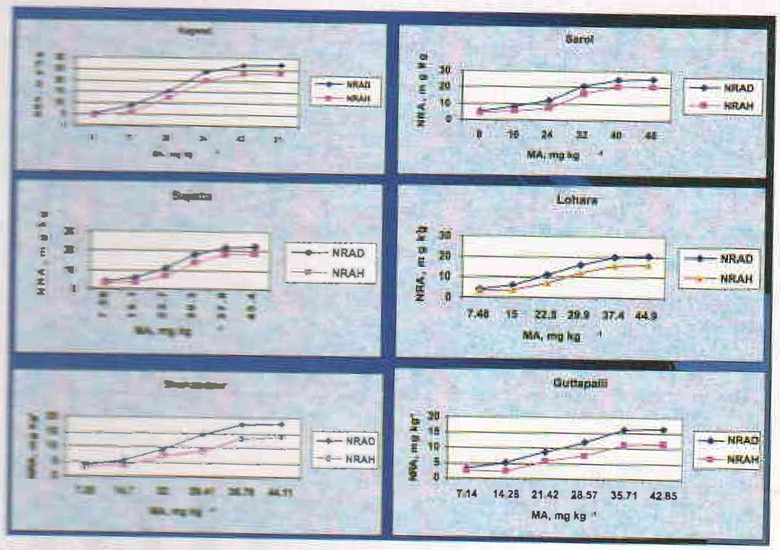


Fig.7. Non-recoverable Cd at different metal additions

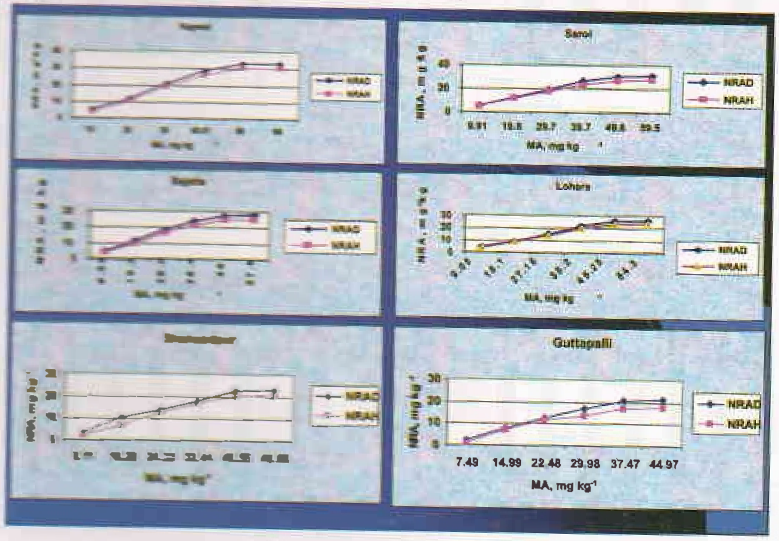


Fig. 8.Non-recoverable Pb at different metal additions

7.4. Effect of Organic Matter on Cd Toxicity

A pot culture study was also undertaken to evaluate the effect of Cd, with or without spent wash (TOC 37 g L^{-1}) as a source of organic matter, on the yield and quality of spinach in a swell-shrink soil of Raichur (Vertisol; pH 8.0, CEC 72 cmol (p+) kg^{-1}). Spinach exhibited some symptoms of toxicity like stunted growth, interveinal chlorosis, etc. at higher level of Cd loading. Dry matter yield of spinach decreased very slightly with Cd levels up to 20 mg kg^{-1} soil, beyond which it decreased very sharply and above 60 mg kg^{-1} level, there was drastic reduction (Fig. 4). The trend was almost similar in cases where spent wash was added along with Cd (Babejova *et al.*, 2001). However, the supply of organic matter and nutrients through spent wash increased the dry matter yield of spinach and thus negated the adverse effect of higher does of Cd to some extent. For example, the dry matter yield of spinach with 60 mg Cd kg^{-1} soil amended with 2.5 cm spent wash was almost similar to that of control (Fig. 10).

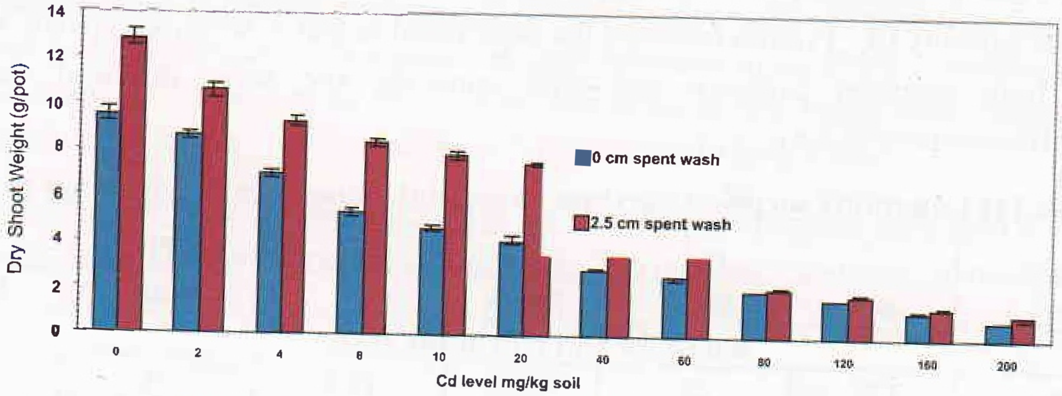


Fig 10. Effect of Cd and Spent wash on dry matter yield (g/pot) of spinach shoot

7.5 Operationally Defined Soil Fractions of Heavy Metals

Cadmium is one of the most potential bio-toxic heavy metals and is considered to be a ve important soil pollutant. The knowledge on distribution of Cd among various chemical forms is prime importance to understand its solubility, mobility and bioavailability(Kaasalainen and Y Halla, 2003). Keeping this in view, soil samples collected from the pots after harvest of spinach cr were fractionated to know the transformation of Cd in various chemical pools in the soils (Cove *et. al.*, 2004)

Cadmium was extracted into the following operationally defined fractions of the soil; wa soluble (distilled H_2O) exchangeable (1.0 M $CaCl_2$), carbonate (1.0 M NaOAc, pH 5); Fe-M oxides (0.04 M NH_4 OH.HCl), organic (0.02 M HNO_3 + 30% H_2O_2; 3.2M NH_4OAc), and resid (con. HF + con. $HClO_4$). Sequential extractions were carried out in triplicate using 1.0 g sampl polyethylene centrifuge tubes. The metal content in the extracts from the soil samples w determined by Atomic Absorption Spectrophotometer.

Some specified treatments of the pot experiment were chosen (control, 10 mg Cd kg^{-1} soil, 40 mg Cd kg^{-1} soil, 40 mg Cd kg^{-1} soil plus 2.5 cm spent wash, 60 mg Cd kg^{-1} soil, 80 mg Cd kg^{-1} soil) for fractionation depending on their significant effect on spinach crop (Fig. 11). In 10 mg Cd kg^{-1} treatment, it was observed that water soluble fraction of Cd was not detected and predominant fraction was Fe-Mn oxide bound Cd (Kabala and Singh, 2001). It indicated the importance of Fe-Mn oxides specially at higher pH values in lowering the activity of Cd in soil solution. Different fractions of Cd present in this treatment followed this order: Fe-Mn oxides bound> exchangeable> residual> carbonate bound> organic bound> water soluble.

Application of 40 mg Cd kg^{-1} soil increased the exchangeable fraction to a great extent, which might have reached to toxic level for plants and yield of the plants decreased tendency. The application of spent wash changed the metal concentrations in soil to varying degrees (Fig. 5). The highest level of Cd was found in exchangeable fraction. This shows that exchangeable Cd was the most abundant fraction in higher levels of Cd treated soil. But application of spent wash helped to maintain exchangeable–Cd level below toxic limit. Fractionation study thus revealed that at higher level of Cd application, exchangeable Cd fraction was dominant. Almost all the fractions were negatively correlated with dry matter yield of spinach crop.

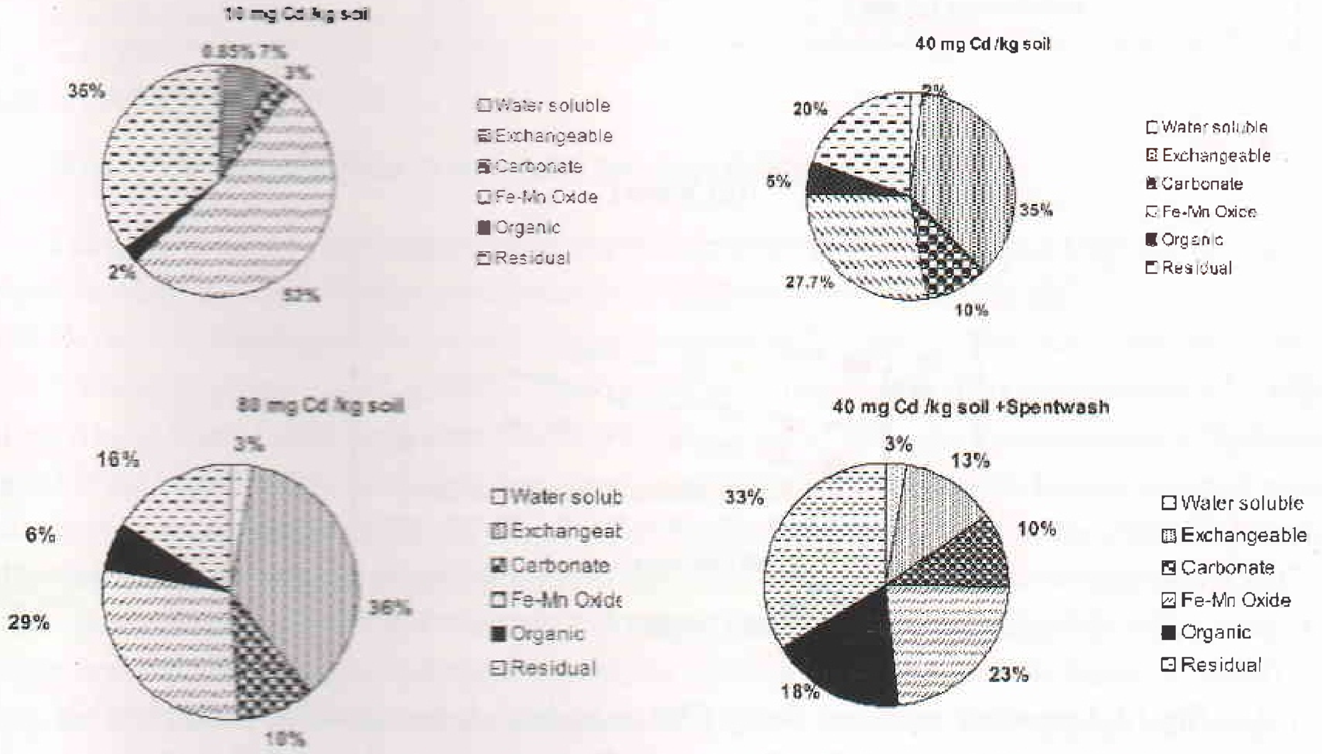
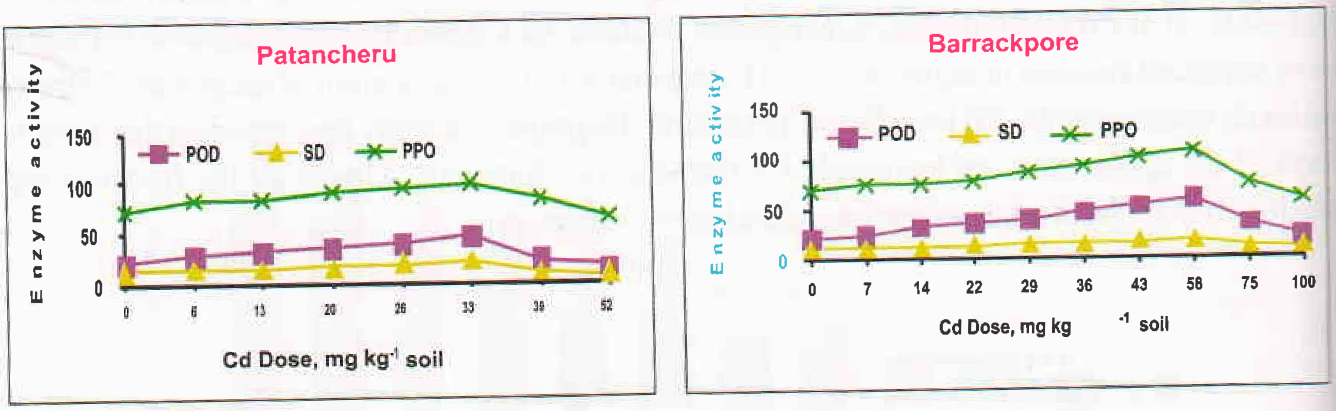


Fig. 11. Distribution of cadmium (mg kg^{-1}) in different fractions of soil growing spinach

7.6. Heavy Metals on Phytometallophore Production and Enzymatic Activities

Peroxidase (POD), succinic dehydrogenase (SD) and polyphenyl oxidase (PPO) activities of young soybean leaves indicated that there was initial stimulation at lower level of Cd addition followed by inhibition (Fig.12). All enzymatic activities got inhibited beyond the Cd dose of 33, 58 and 60 mg kg^{-1} soil in Patancheru, Barrackpore and Jabalpur soils, respectively. These values corroborated perfectly with the extent of yield depression in shoot dry matter yield of soybean. Likewise, phyto-metallophore production was stimulated at lower levels of heavy metals followed by inhibition at higher levels of heavy metal addition (Table 10 & 11).



(a) Patancheru

(b) Barrackpore

(c) Kheri

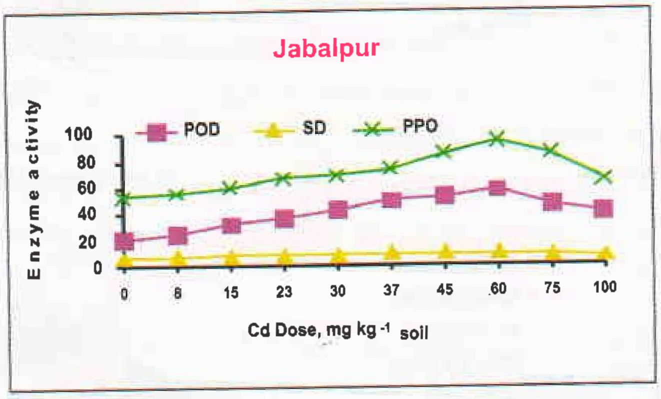


Fig.12. Enzymatic activities (mg/g FW) in soybean leaves at different levels of Cd contamination in (a) Patancheru, (b) Barrackpore, and (c) Jabalpur soils

Table 12. Cd on the release of phytosiderophores and consequent changes in pH after 24 hours

Cd Dose	**Patancheru**		**Jabalpur**		**Barrackpore**	
	Phenol	**pH**	**Phenol**	**pH**	**Phenol**	**pH**
0	15.0	6.38	6.6	6.56	4.8	6.62
13	12.9	6.15	4.8	6.42	8.7	6.25
26	13.3	6.10	28.2	5.85	11.8	6.34
39	16.0	6.32	10.8	6.58	11.5	6.38
52	8.5	6.57	8.1	6.62	2.4	6.76

Blank pH = 6.85; Phenol= uM /g FW

Table 13. Cd on the release of phytosiderophores and consequent changes in pH after 48 hours

Cd Dose	**Patancheru**		**Jabalpur**		**Barrackpore**	
	Phenol	**pH**	**Phenol**	**pH**	**Phenol**	**pH**
0	16.8	6.28	8.4	6.52	6.6	6.62
13	14.7	6.05	6.6	6.38	10.5	6.15
26	15.1	6.00	30.2	5.32	13.6	6.34
39	17.8	6.23	12.6	6.43	13.3	6.42
52	10.3	6.48	9.9	6.55	4.2	6.72

Blank pH = 6.85; Phenol= uM /g FW

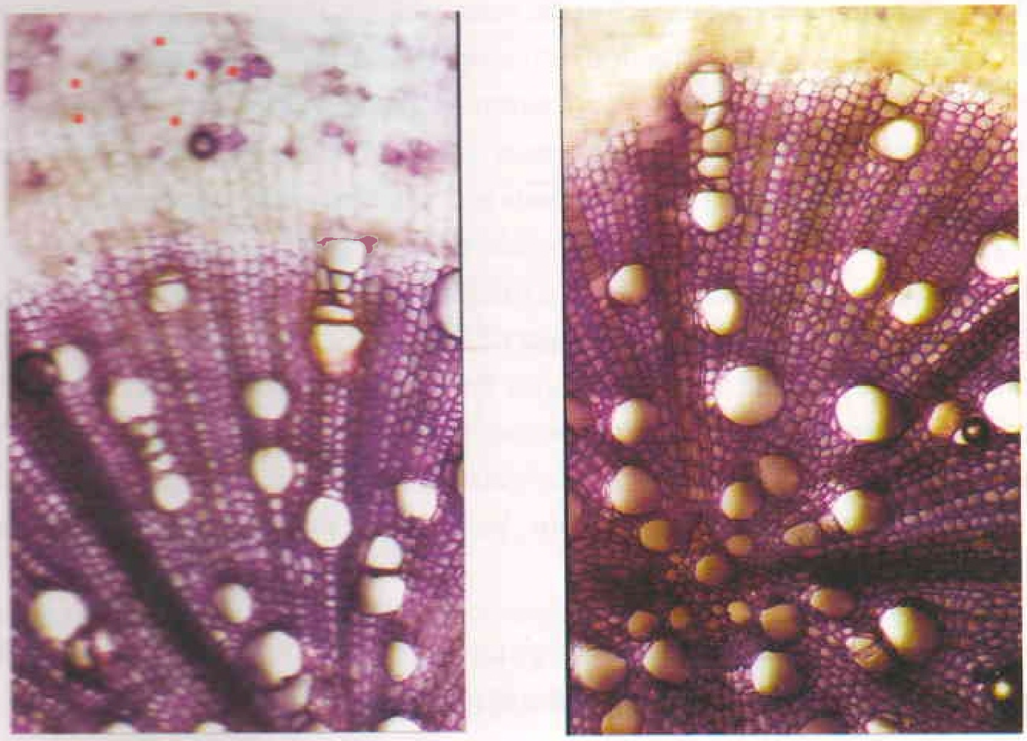
8. Heavy metal pollution in soils and phytotoxicity

The phytotoxicity due to cadmium (Cd), chromium [Cr (VI)] and nickel (Ni) and the likely contamination of the food chain resulting from their addition from low to very high levels to a swell-shrink clayey soil (Haplustert) in spinach (*Spinacia oleracea* L.), maize (*Zea mays*), Italian Napier grass (*Pennisetum purpureum L.*) Typha (*Typha latifolia L.*) and castor (*Ricinus communis L.*) was studied. Above 80mg Cd kg^{-1} soil, there was very slow growth of spinach after germination. Spinach crop suffering from severe Cd toxicity had small roots and narrow yellowish leaves, covered with small necrotic spots. Higher levels of Cd inhibited the growth and biomass of the crop. However, application of spent wash alleviated the toxic effect of Cd to some extent. The concentration of Cd in plant parts increased when Cd was applied singly but decreased considerably when used in combination with spent wash. Cd concentration in spinach root ranged from traces (control) to 120mg kg^{-1} dry matter and was directly related to soil Cd concentration. At 40mg kg^{-1} soil, yield of spinach was reduced to 38% of control plants.

At levels of more than 75 mg Cr (VI) kg^{-1} soil for maize there was virtually no growth after germination, whereas 25 mg Cr (VI) kg^{-1} soil hindered the germination of spinach crop. Initial symptoms of Cr (VI) toxicity appeared as severe wilting of the tops of treated plants. Maize plants suffering from severe Cr (VI) toxicity had smaller roots and narrow brownish red leaves covered with small necrotic spots. In spinach, severe chlorosis was observed in leaves. Higher levels of Cr (VI) inhibited the growth and dry-matter yield of the crops. However, application of city compost alleviated the toxic effects of Cr (VI). The concentration of Cr (VI) in plant part increased when Cr (VI) was applied singly but decreased considerably when used in combination with city compost. There was evidence of an antagonistic effect of Cr (VI) on other heavy metals (Mn, Cu, Zn, and Fe) concentration in plant tops. Thus, when Cr (VI) concentration increases, in maize roots ranged from traces (control) to 30 mg kg^{-1} and were directly related to soil Cr (VI) concentration. At 25 mg Cr (VI) kg^{-1} soil, yield of maize was reduced to 41% of control plants, whereas in spinach, 10 mg Cr (VI) kg^{-1} soil caused a 33% yield reduction (Adhikari and Singh, 2007). The maize top (cereal) is less effective in accumulating Cr (VI) than spinach (leafy vegetables).

The phytotoxicity due to nickel (Ni) and its accumulation in selected plant species resulting from its addition from low to high levels to a swell- shrink clayey soil (Haplustert) was studied in a pot culture experiment. Twelve levels of Ni (0,1.5,3.75,7.5,15,30,50,75,100,150,200 mg/kg soil) were applied. Napier grass (Pennisitum purpureum L.) of family Graminae and Typha (Typha latifolia L.) of family Typhaceae were taken as test plants. Three consecutive cuttings (1st cutting, 2nd cutting and 3rd cutting) of each crop were taken and analyzed. Recorded weights of the crops were significantly reduced above 75 mg Ni/kg soil and 50-mgNi/kg soils for napier and typha respectively. At ther higher Ni levels, above 75mg Ni/kg and 50-mgNi/kg soils for napier and typha respectively, chlorosis symptoms were observed on the leaves of the crops. Regarding Ni accumulation capacity, based on a value, napier grass (a= 0.74) accumulates more Ni than typha plant (a= 0.68). Based on β values, 0.18 and 0.16 for napier and typha respectively, those plants were of excluder type ($\beta<1$).

At the higher Ni levels, above 200 mg Ni kg^{-1} soil, reduced growth symptom was recorded in castor. The concentration of Ni in plant parts increased with increasing dose of applied Ni. Ni concentration in castor root ranged from traces (control) to 455 mg kg^{-1} and was directly related to soil Ni concentration. At 200 mg Ni kg^{-1} soil, dry matter yield of castor was reduced to 10% of control plant. Significant changes were observed in the roots of castor treated with higher levels of Ni against control. The roots treated with Ni showed a decrease in number of cells in the cortex region. It also appeared that the cortex region consisted of elongated parenchymatous cells instead of the normal parenchymatous tissue as in the control plant. Regarding Ni accumulation capacity, castor plant was recorded as an accumulator (=0.11 and =1.10). Results depicted that photosynthesis and chlorophyll content decreased with increasing concentration of Ni. To combat the stress situation, respiration rate of castor plant increased with increasing level of Ni. Moreover, enzyme assay also showed that at higher doses of Ni, activity of the enzymes viz., NR (Nitrate Reductase), POD (Peroxidase) and SD (Succinate Dehydrogenase) decreased. A laboratory study was also conducted on the experimental soil to know the different operationally defined fractions of Ni, which control the availability of Ni to castor. Different fractions of Ni present in this soil followed this order: Residual> Fe-Mn oxides> carbonate > organic >exchangeable> water soluble


(A) 180 mg Ni/kg

(B) Control

Plate 1. Effect of nickel on anatomical changes in the root of castor (A) treated with180 mg Ni/kg (red line indicated elongation of cell wall) and (B) control

9. Impact of pollutant elements on vegetables growing in sewage-sludge-treated soils

The practice of irrigating crop plants with sewage sludge and effluents of industries is long established. These additions have increased the concentration of pollutant in soils, which is a matter of great concern because they enter continuously into the food chain. This practice directly or indirectly affects human health. Under these circumstances, it is necessary to assess the manner and extent to which agricultural plants are affected by sewage sludge and the effluents of different types of industries. Aquatic plants have the ability to accumulate nutrients and accelerate nutrient cycling in the environment. These plants are also able to remove metals from water through processes of biosorption and metabolism – dependent bioaccumulation. In an aquatic environment, the uptake of a metal by a living organism depends on the concentration and chemical form of the metal. The rate of the uptake on several factors such as salinity, temperature, alkalinity, and oxygen concentration in water.

Cultivation of vegetables and other crops with sewage water is a matter of serious concern because it contains heavy metals and contaminated with pathogens such as coliform bacteria. A micro plot filed experiment was conducted at the Farm of IISS, Bhopal for three years to determine the effect of continuos sewage irrigation on crop produce. Representative crops of human consumption from different families like Leguminaceae (*Palmarosa*), Cruciferae (*Mustard*), Malvaceae (*Sunflower*), Graminae (*Lemongrass and wheat crops*), Zingiberaceae (*Ginger*), Alliaceae (*Turmeric*) were grown in different plots and irrigated with sewage water and tap water as control (Ajay *et al.* 2003). Based on economic yield characteristic and crop growth behavior, these crops have been classified into three groups viz. tolerant, semi tolerant and susceptible crops. From each group three crops were selected irrespective of families to show its characteristics behavior. A perusal of data presented in the figures showed the physiological and biochemical differences among these three groups of the crops. It can be concluded from the results that cultivation of crops with continuous application of sewage water irrigation could cause some adverse effect on quality and yield in susceptible and semi-tolerant crops, however, in tolerant care must be taken for food purposes.

The following tables showed the total plants screened for tolerant, susceptible and semi-tolerant category, mainly based on yield characteristics:-

Table 14. Effect on continuous sewage application on some plant parameters and heavy metal composition of some selected crops

Crops	NO_3(µM/g DW)	o-DHP (ppm)	Heavy metals content (ppm)				
			Cd	Pb	Ni	Cu	Zn
Ginger -C	2.23	0.12	02	08	07	20	30
Ginger -S	3.26	0.05	18	45	35	35	45
Lemongrass -C	4.54	0.59	03	09	06	25	35
Lemongrass -S	8.54	0.47	30	75	60	60	69
Mustard -C	3.25	0.80	02	07	05	23	28
Mustard -S	5.35	0.66	19	60	45	50	50
Palmarosa -C	0.43	1.25	03	08	04	20	20
Palmarosa -S	0.56	1.05	20	30	30	32	40
Sunflower -C	4.28	0.75	02	06	06	22	23
Sunflower -S	8.90	0.55	12	25	32	40	45
Turmeric -C	0.11	1.20	02	04	03	18	25
Turmeric -S	0.16	1.11	13	28	25	39	40
Wheat -C	5.28	1.40	02	09	06	25	20
Wheat -S	9.30	1.30	08	30	40	35	42

*C=Control, *S=Sewage Treated

10. Remediation techniques

Soil acts as a good sink for most of the pollutants but their indiscriminate disposal is causing soil pollution and environmental hazards. An unfortunate consequence of industrialization has been the contamination of soil, sediment and water resources with toxic metals and metalloids. Additional soils and sediments have been contaminated by metal – containing sewage sludge, metal working and plating products, heavy metal based paints and coatings, and some pesticides and fertilizers (Alloway, 1995). Remediation of sites contaminated with toxic metals is particularly challenging. Unlike organic compounds, metals cannot be degraded, and the cleanup usually requires their removal. The metal removing process often employs stringent physicochemical agents which can dramatically inhibit soil fertility with subsequent negative impacts on the ecosystem. Chemical and phytoremediation have been proposed as cost effective, environmental friendly alternative technologies. Different chemical treatments brought about the changes in the speciation and extractability of heavy metals and their availability to plants. Suitable chemical treatments need to be developed for specific location. For phytoremediation process, a great deal of research indicates that plants have the genetic potential to remove many toxic metals from the soil.

Progress in the field is hindered by a lack of understanding of complex interactions in the rhizosphere and plant-based mechanisms that allow metal translocation and accumulation in plants. Hence systematic studies need to be carried out to identify the metal hyper-accumulators, plants capable of accumulating extraordinarily high metals levels, and specific and effective chemical treatments to minimize soil pollution and sustaining agricultural production. Current remediation methods applicable to soil contaminated with heavy metals are expensive, environmentally invasive and labor intensive. They are based primarily on civil – engineering techniques that often involve excavation of the contaminated soils, and often require additional effort, time, and money to restore the site to a healthy condition. A remediation technique that is low cost, environmentally sound, and equally protective of human health and the environment would be a valuable alternative to current remediation methods. Soil amendments have been used both in agriculture and remediation for a long time (Illera *et al*., 2004, De Varennes and Queda, 2005). Agriculture has relied on soil amendments such as lime, gypsum, and fertilizers to alter soil physical and chemical properties to optimize plant yield. Although these amendments and application rates do not often translate directly to risk reduction in contaminated soils, much of our understanding of the chemical behaviour of metal contaminants in soils derives from this research. Soil amendments are also used in certain forms of traditional remediation, albeit with different ends. Phytorestoration is an amalgam of these two technologies that uses our understandings of both the remediation and agricultural areas to produce a cost-effective technique that safeguards both human health and the environment and helps establish viable and sustainable ecosystems. The fundamental premise of many in situ remediation techniques is to reduce the relative bioavailability of a metal in the soil by the addition of soil amendments and by the establishment of biological communities which further immobilizes the metals in soil. Soil excavation and land filling is the most common remediation method for metal-polluted soils. But it is extremely environmentally disruptive and expensive. Ideally, plants should not accumulate contaminants in above-ground plant tissues which could be consumed by humans and cause harm. Lime materials, containing various proportions of carbonates, hydroxides, and oxides of Ca and Mg, are used to raise soil pH as a normal farming practices to increase crop production. Because the solubility of metals usually increases with decreasing soil pH, most investigations attempting to reduce the availability of metals to plants have concentrated on liming. But other metals in anionic forms, such as molybdate, arsenate and chromate may become more available with increasing pH. So combined application of lime and organic matter may be effective (Renella *et al*. 2004).

10.1 Remediation of cadmium pollution in soils by different amendments

A column study was conducted to determine the effect of city compost, lime, gypsum, and phosphate on cadmium (Cd) mobility in three well-recognized benchmark soils of India [viz., Islamnagar (Vertisol), (Amarpur) (Inceptisol), and Khala (Alfisol)]. Columns made of PVC were filled with soil treated with different treatment doses [viz., 0.5% city compost, 1% city compost, 2% city compost, 2.5 t lime/ha, 5t lime /ha, 2.5 t lime/ ha +0.5 % city compost, 2.5 t gypsum /ha, +0.5% city compost and 100 kg P_2O_5/ha as potassium phosphate (KH_2PO_4). The columns were leached with 100mg L^{-1} Cd under saturated condition. The amount of water moving through the soils was measured as the pore volume. A delayed breakthrough curve (BTC) of Cd in the presence of lime has been observed in all the studied benchmark soil series. Among the treatments, lime application reduced the movement of Cd from surface soil to lower depth of soil of Islamnagar, Amarpur and Khala series, respectively. Explanation from reduced Cd mobility in limed soil can be derived from pH changes of soils. In comparison to control soil, phosphate application caused 6, 21 and 30% more retention of Cd in surface soil in Islamnagar, Amarpur, and Khala series, respectively. Combined application of lime and city compost reduced the movement of Cd in the soil profile. It appears that organic matter controls the sorption of Cd in soils. The amount of Cd sorbed increased with increasing organic carbon content, but gypsum application may leach Cd beyond the root-zone depth. A rapid breakthrough curve was observed under gypsum-treated soils. Retardation factor revealed that a somewhat lower degree of Cd retention occurred in the Khala series, which might possibly be attributed to less clay content and low pH. Overall, the column study indicated that total Cd accumulation occurred up to depths of 5-7.5 cm, 7.5-10 cm, and 10-15 cm in soils of Islamnagar, Amarpur, and Khala series, respectively(Adhikari and Singh, 2008).

10.1.1 Spent wash application

The phytotoxicity due to cadmium (Cd) and its likely contamination of food chain resulting from its addition from low to very high levels to a swell-shrink clayey soil (Haplustert) in spinach (*Spinacia oleracea L.*) was studied. Twelve levels of Cd (0, 2, 4, 8, 10, 20, 40, 60, 80, 120, 160, 200 mg kg^{-1} soil) were applied singly and in combination with two doses (0 and 2.5 cm) of spent wash (Distillery effluent). Above 20 mg Cd kg^{-1} soil inhibited the growth of plants and thus decreased plant biomass productivity. The concentration of Cd in plants increased when Cd was used singly but decreased considerably when used in combination with spent wash. Dry matter yield of spinach was negatively affected (20% reduced) starting from as low as 10 mg kg^{-1} soil level, but with the application of spent wash spinach crop can tolerate higher levels of Cd up to 60 mg kg^{-1} in a Vertisol. Spent wash application can be recommended to prevent the Cd toxicity in spinach grown in soil (Adhikari *et al.* 2005).

10.2 Bioremediation techniques

Bioremediation to reduce the heavy metal load in agricultural field is an accepted practice in most of the countries.It includes both the phytoremediation and microbial decontamination of soil.

10.2.1 Phytoremediation techniques

Phytoremediation, the use of plants for environmental restoration, is an emerging clean up technology. Phytoremediation can be defined as the process of utilizing plants to adsorb, accumulate, detoxify and/or render harmless, contaminants in the growth substrate (soil, water and air) through physical, chemical or biological processes.

Plant metal uptake

Plants extract and accumulate metals from soil solution. Before the metal can move from the soil solution into the plant, it must pass the surface of the root. This can either be a passive process, with metal ions moving through the porous cell wall of the root cells, or an active process by which metal ions move symplastically through the cells of the root. This latter process requires that the metal ions traverse the plasmalemma, a selectively permeable barrier that surrounds cells. Special plant membrane proteins recognize the chemical structure of essential metals; these proteins bind the metals and are then ready for uptake and transport. Numerous protein transporters exist in plants. For example, the model plant thale cress (*A. thaliana*) contains 150 different cation transporters and even more than one transporter for some metals. Some of the essential, nonessential and toxic metals, however, are analogous in chemical structure so that these proteins regard them as the same. For example arsenate is taken up by P transporters. For root to shoot transport these elements are transported via the vascular system to the above-soil biomass (shoots). The shoots are harvested, incinerated to reduce volume, disposed of as hazardous waste, or precious metals can be recycled (phytomining). Different chelators may be involved in the translocation of metal cations through the xylem, such as organic acid chelators malate, citrate, histidine. Since the metal is complexed within a chelate it can be translocated upwards in the xylem without being adsorbed by the high cation exchange capacity of the xylem.

Phytodecontamination is a subset of phytoremediation in which the concentration of the contaminants of concern in the soil is reduced to an acceptable level through the action of plants, their associated microflora and agronomic practices. The process of phytodecontamination is achieved by *phytoextraction, phytodegradation, rhizofilteration, phytovolatilization, and rhizo (sphere) degradation.*

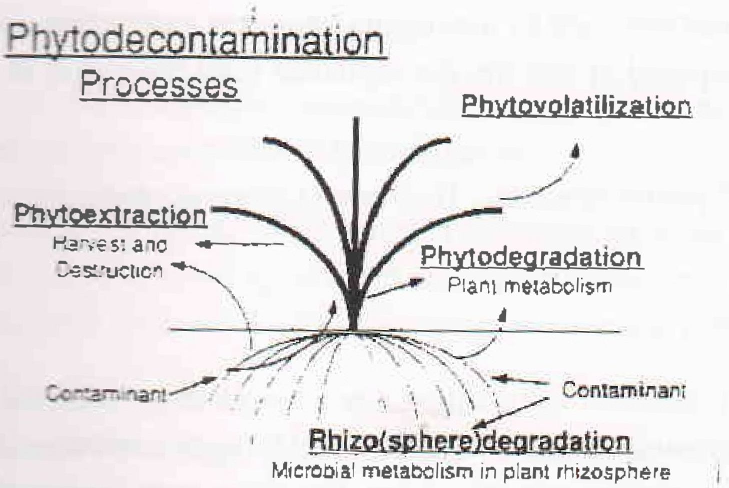


Plate 2. Phytoremediation

Phytoextraction (Phytoaccumulation)

It is the name given to the process where plant roots take up the metal contaminant from the soil and translocate them to their above ground plant tissues. Once the plants have grown and absorbed the metal pollutants, they are harvested and disposed off safely. This process is repeated several times to reduce contamination to acceptable levels. In some cases it is possible to recycle the metals through a process known as phytomining, though this is usually reserved for use with precious metals. Metal compounds that have been successfully phytoextracted include zinc, copper, and nickel, but there is promising research being completed on lead and chromium absorbing plants. Hyperaccumulator plant species (species which absorb higher amounts of pollutants than most other species) are used on many sites due to their tolerance of relatively extreme levels of pollution.

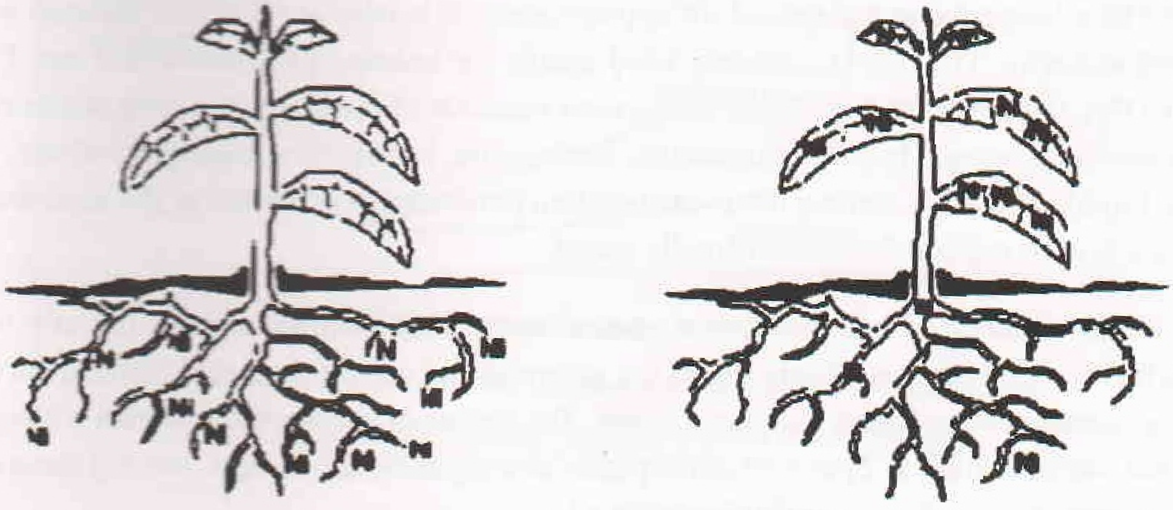


Plate 3. Nickel accumulation by plant

Nickel is removed from soil by moving up into plant roots, stems, and leaves. The plant is then harvested and disposed of and the site replanted until the nickel in the soil is lowered to acceptable levels

There are two types of phytoextraction. They are (1)Natural phytoextraction and (2) Induced phytoextraction.+

Natural phytoextraction

It is usually conducted by planting (or transplanting) selected plant species in the contaminated soil. These plants are grown under normal farming conditions (fertilized and irrigated as necessary) until they reach their maximum size. The above ground parts of the plants containing the contaminants are then harvested and disposed off appropriately. The plants are highly specialized, occur naturally, and can tolerate very elevated concentrations of metals that would be toxic to other plants. Typically, these plants are small, have a small and shallow root system, and grow relatively slowly.

Induced phytoextraction

In non hyperaccumulators plants, factors limiting their potential for phytoextraction include small root uptake and little root-shoot translocation of metals. Methods making the use of metal-mobilizing agents have been proposed specifically to overcome these limitations. Following this approach, a high biomass crop is grown on the soil requiring remediation. It is conducted by growing selected fast-growing plants in the contaminated soil. Throughout the growth period, amendments are added to the soil to increase availability of metals to the plants. When the plants are mature, inducing agents (chemicals) are used to trigger accumulation of metals from the soil. The plants are then harvested and disposed off appropriately. It is possible that two harvests will be conducted annually. The most commonly used agents for induced phytoextraction are: EDTA, DTPA, CDTA and Citric acid etc.There are several methods of contaminated crop disposal after phytoextraction process. They are composting, compaction, incineration, ashing, pyrolysis, direct disposal, liquid extraction. Among them, incineration (smelting) is proposed as the most feasible, economically acceptable and environmentally sound.

Phytoextraction offers an efficient, cost-effective, and environmentally friendly way to clean up heavy metal contamination. Plants are grown in situ on contaminated soil and harvested after toxic metals accumulate in the plant tissues. The degree of accumulation varies with several factors, but can be as high as 2 per cent of the plants' aboveground dry weight, leaving clean soil in place that meets or exceeds regulatory cleanup levels.

Response of plants to heavy metals

Three basic types of plants depending upon the response of plants to heavy metals may be classified as (1)Excluders (2)Indicators and (3)Accumulators.

Excluders: These plants have low uptake of the metal at quite high external metal concentrations. They have some kind of barrier to avoid uptake, but when metal concentration becomes too high these barrier losses it's function probably due to toxic action by the metal and the uptake massively increases.

Accumulators: These plants have high concentrations of metals at very low external metal concentrations. These plants have certain detoxification mechanisms within the tissue which allow the plant to accumulate such high amounts of metals. At high external concentrations however, these plants don't increase their uptake probably due to *competition between metal ions at the site of uptake.*

Indicators: These plants have a tissue concentration reflecting the external metal concentration, increasing the uptake linearly with increasing metal concentrations in the external medium.

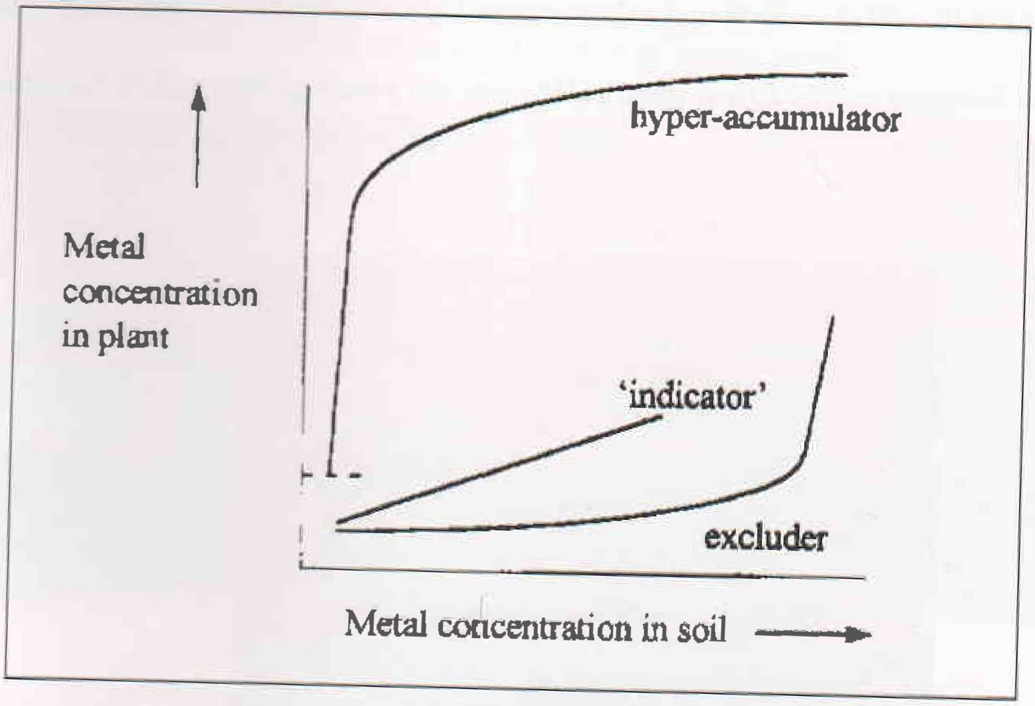


Plate 4. Plant classification based on metal accumualtion

10.2.2 Tolerance limits of some plants to heavy metals

Green house experiments were carried out to investigate the effect of Cd (0, 25, 50, 75, 100) Pb (0, 25, 50, 75, 100, 200, 300), Ni (0, 25, 50, 75, 100, 200, 300), and Cr (0, 25, 50, 75, 100) on karanj (*Pongamia pinnata L.*) (Plate 5 to 9) crop in swell-shrink clayey soil. Experimental results revealed that karanj plant was grown well in the Pb contaminated soil. Growth of the plant was not affected by different Pb doses. Plant was healthy and followed the similar trend of growth like control. At lower doses of Pb, growth of the plant was higher than control. It may be attributed to higher exchange power of Pb because of higher electronegativity, some other nutrients element might release in soil solution in this process and helped in good growth. The results of plant growth parameters of this experiment were supported by some physiological parameters of the plant. Leaf area (4.1 to 5.2 cm^2) and height of the plant (22 to 25 cm) were not affected by the application of higher doses of Pb (up to 300 mg Pb kg^{-1} soil). Photosynthesis is the key to dry matter production and increasing the photosynthetic efficiency is the most important way of increasing productivity. Of all aspects of plant metabolism, photosynthesis shows the most prominent variation under the dictates of the immediate environment. The net photosynthesis rate of karanj plant varied between 10.5 mol $m^{-2}s^{-1}$ to 14.32 mol $m^{-2}s^{-1}$. Even at higher levels of Pb, chlorophyll content was not affected. It is attributed to, Pb as most of the heavy metals are absorbed by the plant but are generally dumped into vacuoles or in cell wall in order to make them physiologically inactive or non-functional.

Jatropha (*Jatropha curcus L*) and datura (*Datura Linn.*) were grown well in Ni contaminated soil. Application of Ni at lower doses below 400 mg Ni kg^{-1} increased growth of the plants (plate

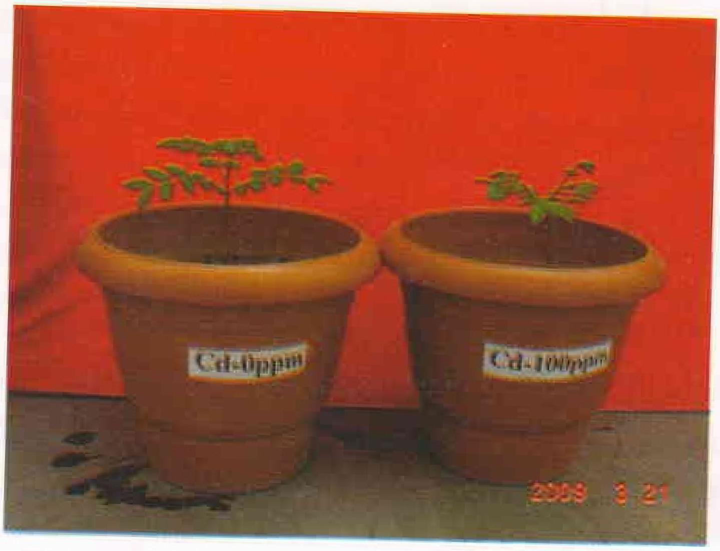


Plate 5. Effect of cadmium on growth of karanj plant

10). Number of leaves and height of the both the plants were not affected by the application of higher doses of Ni (up to 800 mg Ni kg^{-1} soil) (plate 11). Low concentrations of Ni in the substrate stimulate the germination and growth of the crop. Ni is required as metal component in urease enzyme in higher plants and helps in nitrogen metabolism. Growth reduction may be, generally linked to a loss of cellular turgor resulting in either a decreasing of miotic activity and or an inhibition of cell elongation.

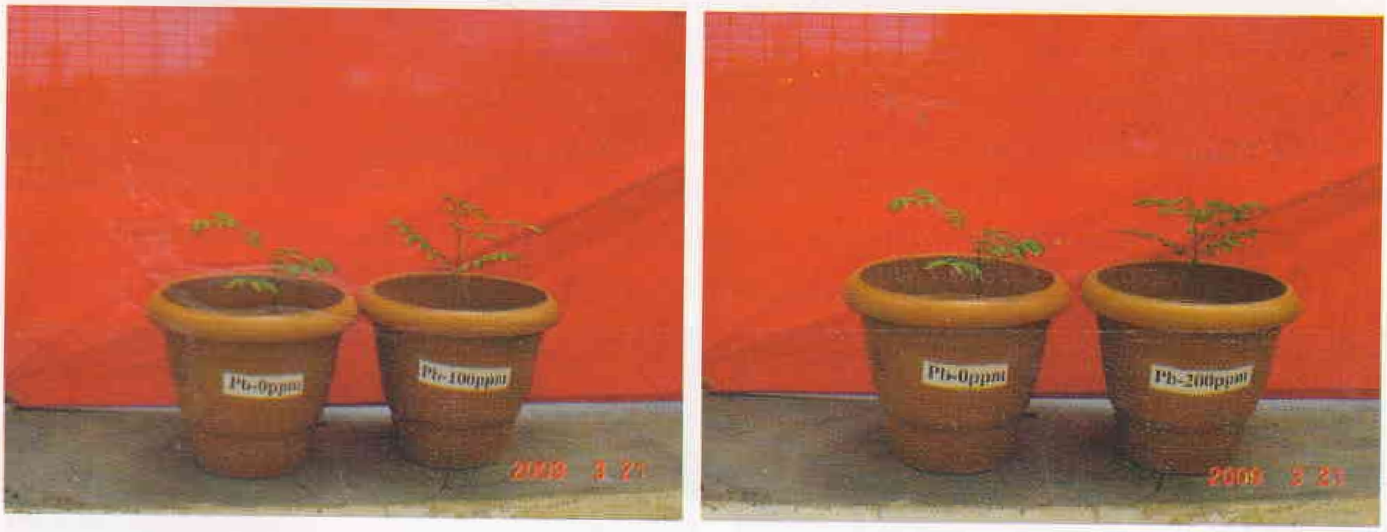


Plate 6. Effect of Lead on growth of karanj plant

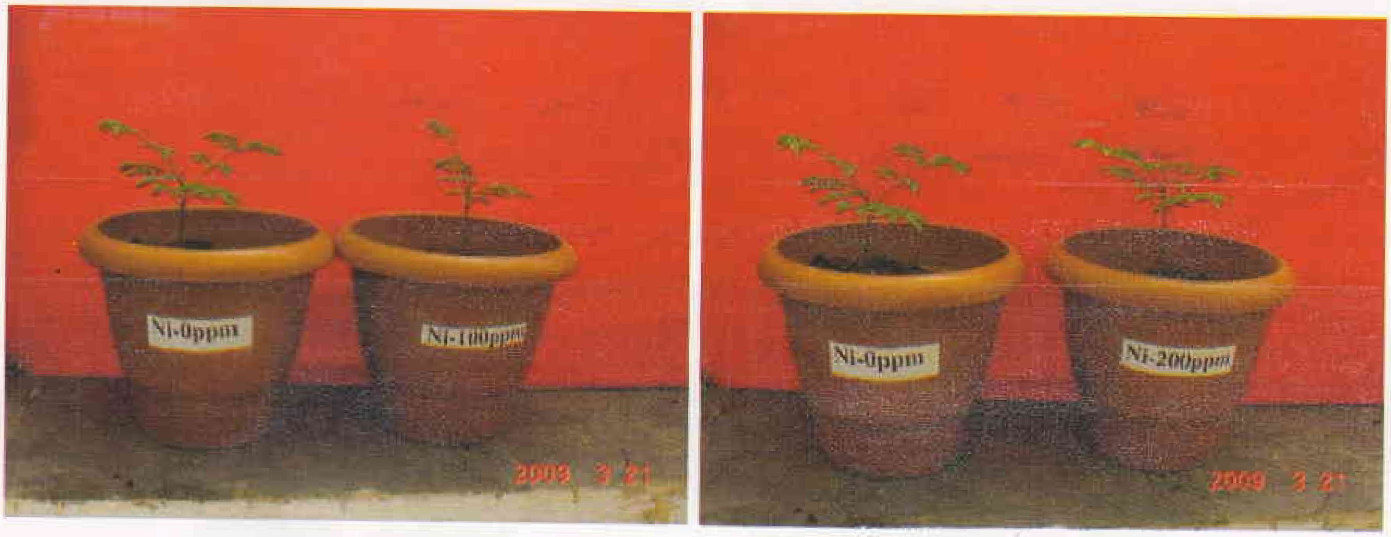


Plate 7. Effect of nickel on growth of karanj plant

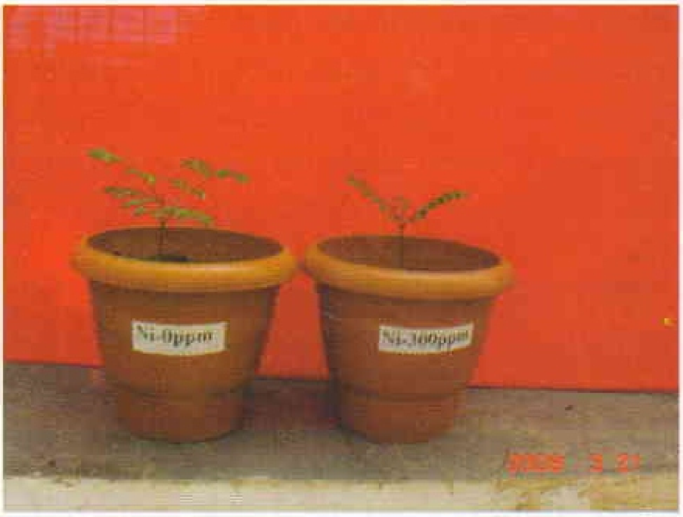


Plate 8. Effect of nickel on growth of karanj plant

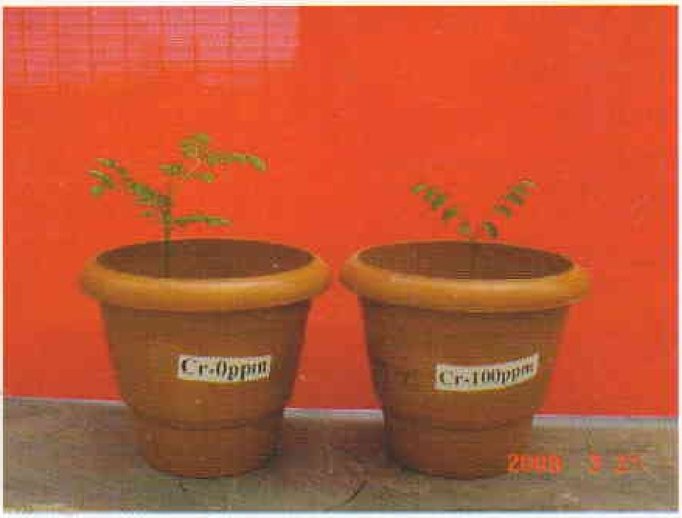


Plate 9. Effect of chromium on growth of karanj plant

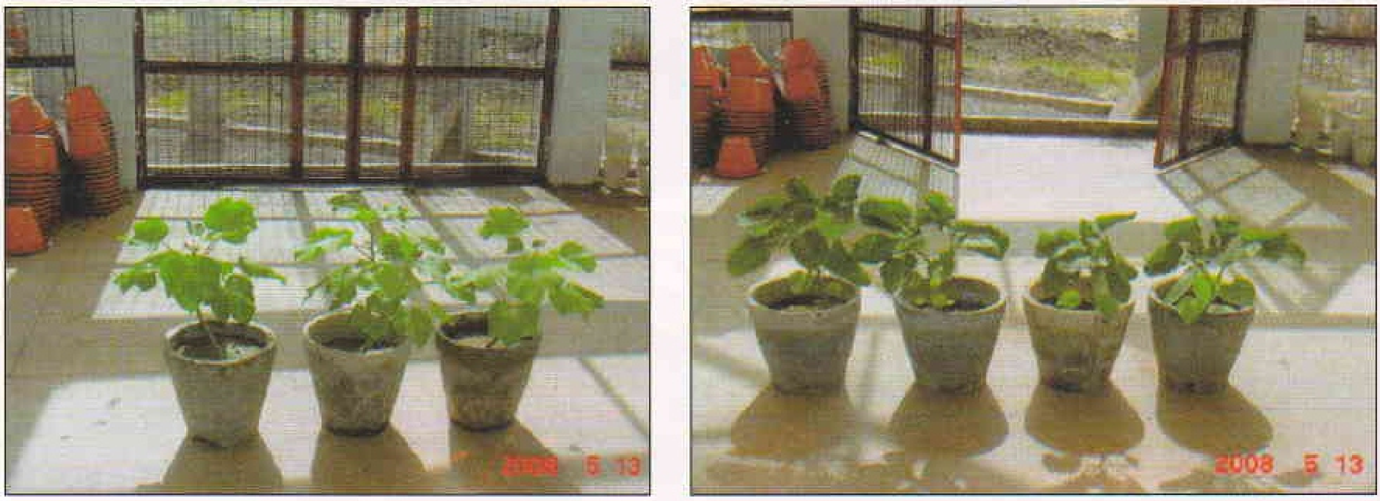


Plate 10. Effect of Ni (0,100,200 ppm) on Jatropha and Datura Plants

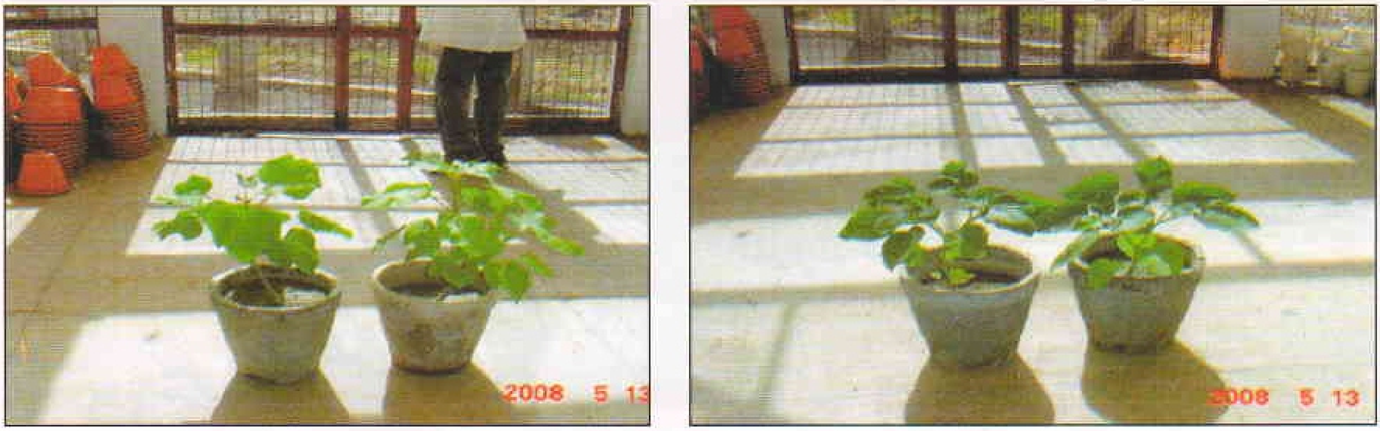


Plate 11. Effect of Ni (600 & 800 ppm) on Jatropha and Datura Plants

10.2.3 Phytoremediation with floriculture plants

Several agricultural lands in the periurban areas have been contaminated with heavy metals due to vehicular pollution, industrial activities such as smelting, mining, electroplating, battery, tanneries, distilleries, etc and agricultural practices such as application of pesticides and chemical fertilizers (particularly phosphatic fertilizers) and use of sewage water. Therefore, the agricultural practices in periurban areas are under scanner due to potential threat of entry of heavy metals to food chain through various crops primarily vegetables grown on fields with these wastes. In a developing country like India preventing use of heavy metal spiked waste water in agriculture is next to impossible. The most plausible way is to develop and apply remediation technology to decontaminate the polluted soils. Among the remediation techniques, phytoremediation has been proved to be the best. The most viable and remunerative alternative could be use of non-edible crops for phytoremediation which will prevent the entry of heavy metals through food chain. Brassica a known oilseed crop is known world wide for its remediation potential, but its use is limited due food chain contamination. Hence the phytoremediation potential of three floriculture plant species i.e., marigold, chrysanthemum, gladiolus vis-a-vis brassica, a known hyperaccumulator) and their suitability for phytoextraction of Cd and Pb was studied (Plate 12). Amongst the four plant species, except marigold all the three plant species tolerated up to 200 ppm of Cd. In marigold, mortality of plants was observed at higher levels of Cd (100 and 200 ppm). However, the application of Pb did not decrease the dry weight significantly. The concentration of Cd in different plant parts of the plants increased with the increase in the level of applied Cd (Ramana *et al.* 2009). Among the four plant species chrysanthemum recorded the highest concentration of Cd followed by marigold, mustard and gladiolus. Chrysanthemum accumulated the Cd mostly in roots (728 $\mu g\ g^{-1}$ DW) compared to stems, leaves and flowers (16 $\mu g\ g^{-1}$ DW). On the other hand, the concentration of Cd in marigold and brassica was higher in leaf and was followed by root, stem and flower. Although chrysanthemum absorbed a large amount of Cd from soil, its movement from roots to shoots was limited. On the other hand, marigold and brassica were less efficient in accumulating Cd, but were more efficient in translocating Cd from root to above ground plant parts. The mechanisms of internal Cd translocation are still not well understood. However, it has been suggested that binding of Cd to the specific root-cell proteins, which form metabolically inactive complexes, results in Cd accumulation in roots. Further, the present study clearly showed that marigold and brassica possessed the typical ability of Cd hyper accumulation characterized by (1) accumulation of Cd in the stems or leaves of the plant exceeding the critical judging standard i.e.,100 $\mu g\ g^{-1}$ DW of a Cd hyper accumulation and (2) by ratios of Cd in the shoots to roots > 1(Table15). The total uptake of Cd was highest in marigold followed by chrysanthemum (Fig 14). Similar to Cd, the uptake of Pb also followed a similar trend (Figure 15). From the study it was found that among the three floriculture plant species, marigold was a hyperaccumulator of Cd as that of brassica and could be safely grown in the soils where the contamination of soils with Cd is up to 50 ppm.

Table 15.The leaf / root ratio of concentration of Cd in marigold and chrysanthemum

Levels of Cd (mg kg^{-1} soil)	Marigold	Chrysanthemum	Brassica
20	1.60	0.32	2.25
50	1.26	0.25	3.25
100	1.24	0.19	1.54
200	——	0.08	1.70

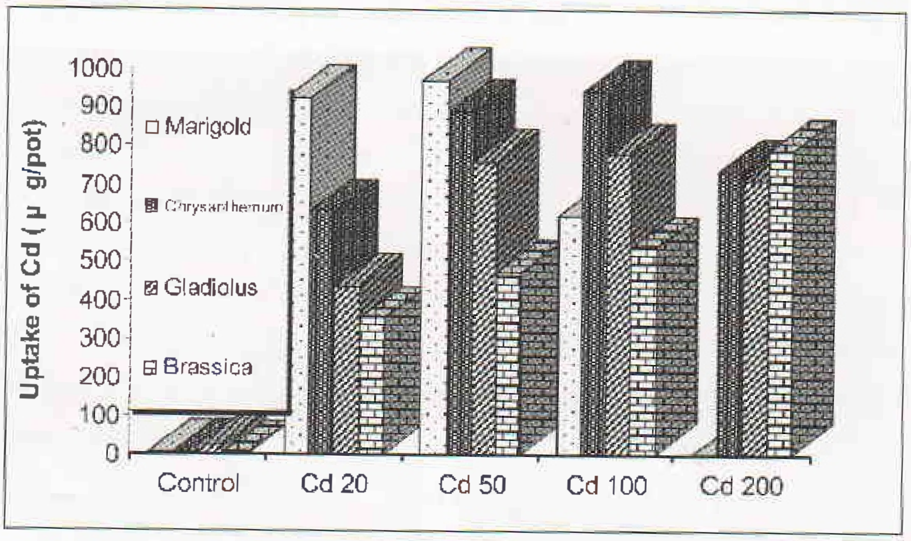


Fig.14. Total uptake of Cd by different plant species

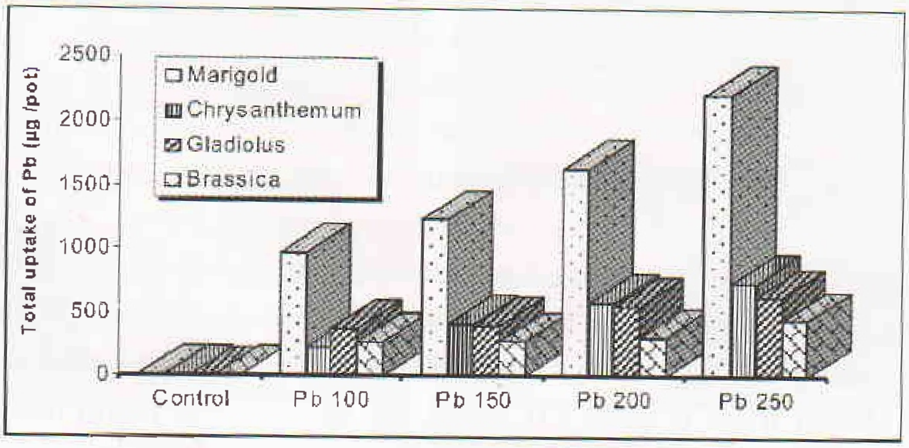


Fig.15. Total uptake of Pb by different plant species

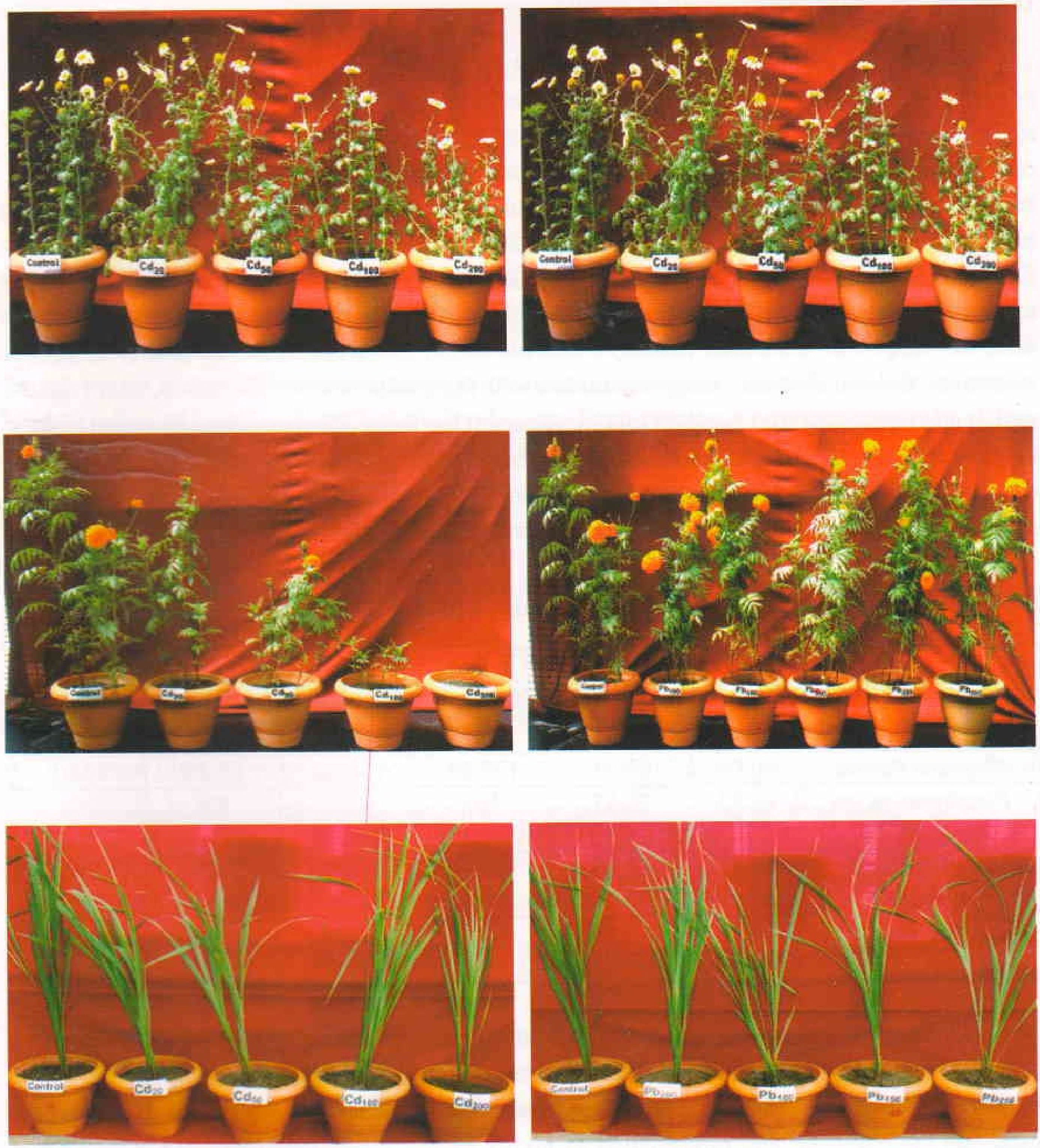


Plate 12. Effect of Cd and Pb on floricultural plants

10.2.4 Microbial decontamination of soils

Soil microbes are capable of binding and accumulating heavy metals in their cells. Soil microbial food chains are thus capable of significant metal biomagnification. A laboratory experiment was conducted at IISS, Bhopal with different microorganisms. *Pleurotus florida* was collected from the division of Biotechnology, Barkatullah University, Bhopal and other species were isolated from sewage water. Those cultures were grown with graded levels of Cd to study the biosorption capacity of these organisms. Results showed that *Pleurotus florida* can be used as bio-filter of heavy metal contaminants in sewage for irrigation purpose. Laboratory experiments were conducted to evaluate the bio-sorption capacity of heavy metals (cadmium and chromium) by different fungi viz. *Pleurotus florida, Fussirum oxiporum, Penicillium sp* and (Aspergillus a*wamorii.* Growth of those fungi was studied with the graded doses of Cd (2.5, 5, 10, 15 and 20 mgL^{-1}) and Cr (2.5, 5, 10, 15 and 20 mgL^{-1}). Amongst the fungi, *Pleurotus florida* sorbed highest amount of heavy metals and could survive at higher levels of heavy metals. So, *Pleurotus florida,* the fungi identified, may be considered as a bio-filter to remove heavy metals from untreated sewage which can be used for irrigation purpose in agricultural field.

Table 15. Biosorption capacity of microorganisms for Cd (mg kg^{-1})

Organism	**Biosorption of Cd (mg kg^{-1}) by fungal organisms**					
	Level of Cd (mg L^{-1}) added in growth media					
	12.5	25	50	75	125	250
Pleurotus florida	40.89	67.73	125.93	122.00	89.36	80.21
Fussisporium sp	15.75	53.57	No Growth	No Growth	No Growth	No Growth
Penicillium digitatum	34.59	63.20	100.99	114.18	No Growth	No Growth
Aspergillus niger	27.98	40.00	No Growth	No Growth	No Growth	No Growth

Soil microbes also possess several mechanisms capable of altering metal bioavailability for uptake into roots. Microbes have been documented to catalyze redox reactions leading to changes in metal mobility in soil and propensity for uptake into roots. A strain of *Xanthomonas maltophyla* catalyzes the reduction and precipitation of highly mobile heavy metal Cr^{+6} to Cr^{+3} which is significantly a less mobile and environmentally less hazardous compound and the same strain was also found to induce the transformation of other toxic metal ions Pb^{+2}, Hg^{+2}, Au^{+3}, Te^{+4}, Ag^{+} and oxyanions, SeO_4. Strains of *Escherichia coli* and *Pseudomonas putida* were subsequently identified. The fungus *Penicillium ochro chloron* has good ability to precipitate a variety of heavy metals including Cu, Ni, Pb, and Cd. In addition, soil microorganisms have been shown to exude organic compounds which stimulate bioavailability and facilitate root absorption of a variety of metal ions including Fe^{+2} and Cd^{+2}.

Bioleaching is another mechanism by which soil can be decontaminated. It is based on metabolic capability of certain microorganisms to solubilize and sequester metals. Bioleaching of metals can be achieved when the leaching bacteria oxidize the insoluble metal salts into soluble forms. Mycorrhizae has been reported in plants growing on heavy metal contaminated soil. In addition, arbuscular mycorrhizal fungi are known to colonize ferns, suggesting a possible role of mycorrhizal associations in the recently reported arsenic hyperaccumulation. Among mycorrhizal fungal species identified in metal rich soils are *Glomus sp*, *Gigaspora sp*, and *Eutrophosphora sp.* Binding of metal to the cell wall of the hyphae has been proposed as a mechanism by which ectomycorrhizal fungi protect the plant from heavy metal toxicity. Several studies indicate inhibition of metal uptake by mycorrhizae. However, it is possible that adapted mycorrhizal fungi may play an important role in hyperaccumulation of some metals and metalloids.

11. Conclusions and Recommendations

Survey of heavy metal contaminated sites

- Heavy metal content of sewage samples was recorded below the toxic level. But heavy use of sewage may cause toxicity in soils in future.
- Soils and plant samples collected from sewage irrigated field showed the accumulation of heavy metals and vegetable crops recorded higher amount than that of cereal crops
- Findings of this study suggest that there should be strict restriction on untreated sewage irrigation to grow crops to reduce the metals entry into human food chain
- The industries may be allowed to throw the effluents into sewage drains only after some pretreatment
- Heavy metal accumulation in the surveyed field (Vertisol) occurred in the root zone of plants, it may create health hazards of human, animals and plants

Chemistry of heavy metal sorption in soils

- Soils of tropical country like India would be more vulnerable to cadmium and chromium toxicity due to higher release of metal with increase in temperature. The results have implications in relation to the fate of Cr (VI) in soils and also highlight that the importance of studying the simultaneous sorption of different elements in soil solution matrix.

- Sorption maxima (b) and the Freundlich constant (K_f) of heavy metals like cadmium, lead, nickel, cobalt etc. were positively correlated to cation exchange capacity (CEC), clay, $CaCO_3$ and pH.
- Cadmium and chromium sorption reactions were exothermic while nickel, cobalt and lead sorption reactions were endothermic in nature.
- Competitive sorption of Cd and Pb revealed that in presence of Pb, the sorption capacity of soil for Cd was reduced.
- Methodology for determination of sink capacity for cadmium and lead based on chemical soil test and phyto-toxicity different methods have been developed. Based on both methods, the sink capacity of soils for Cd and Pb followed the order :Kheri> Barrapor>
- Exchangeable cadmium fraction was found to be dominant in soil solution when applied in higher level.
- Peroxidase (POD), succinic dehydrogenase (SD) and polyphenyl oxidase (PPO) activities of young soybean leaves indicated that there was initial stimulation at lower level of Cd (10 ppm) addition in soil followed by inhibition at higher level(60 ppm). Similar results near also found in case of phytometallophore production by soybean plant.

Bioremediation

- Amongst the fungi, *Pleurotus florida, Fusarium oxiporum, Penicillium digitatum* and Aspergillus *awamorii*, *Pleurotus florida* has been found effective and may be used as a bio-filter to remove heavy metals from untreated sewage which can be used for irrigation purpose in agricultural field.
- *Scopuriaopsis condida* also can be used as a bio-filter to remove heavy metals from untreated sewage water.

Phytoremediation

- Some flowering plants species like, chrysanthemum, gladiolus and brassica may be cultivated in cadmium and lead contaminated soil.

- Marigold and Brassica recorded higher concentration of Cd in the above-ground portion of the plant. Chrysanthemum recorded the highest concentration of Pb followed by Marigold, Brassica and Gladiolus.

Management of heavy metal contaminated sites

- Delayed breakthrough curve (BTC) of Cd in the presence of lime has been observed in both Vertisol and Alfisol
- Amongst the treatments, lime application reduced the movement of Cd from surface soil to lower depth of soil to a large extent resulted in 9% and 45% more retention of Cd in Vertisol and Alfisol respectively
- Phosphate application caused 6% and 30% more retention of Cd in surface soil of Vertisol and Alfisol
- Rapid breakthrough curve was observed under gypsum treated soils. Gypsum application may leach Cd beyond the root-zone depth
- Retardation factor (r=0.96) revealed that a somewhat lower degree of Cd retention occurred in Alfisol

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- Cd accumulation occurred up to 5-7.5 cm and 10-15 cm in Vertisol and Alfisol respectively
- To alleviate the Cd toxicity in soils, application of lime (@ 2.5 t/ha) + 10 t/ha city compost is proved to be the best technique.
- To alleviate the Cr toxicity in soil, either application of 20 t/ha city compost or 4t/ha vermicompost recognized as the best technique.
- Spent wash (@2.5 cm/ha) application alleviate Cd toxicity up to certain limit

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- Phosphate application caused 6% and 30% more retention of Cd in surface soil of Vertisol and Alfisol
- Tolerance limit of *Castor and Sunflower*

Sl. No.	**Element (mg/kg)**	**Castor**	**Sunflower**
1	Cd	160	140
2	Pb	180	160
3	Ni	200	180
4	Cr	20	30

- Enzyme activities such as Peroxidase, Succinic Dehydrogemase etc. were altered by toxic amounts of heavy metals (Cd, Pb, Ni and Cr).
- Induction of enzymatic activity was the first signal of higher concentration of heavy metal accumulation in plants
- Phytotoxicity at an early stage may be evaluated using measurements the enzymatic activities in plants as diagnostic criteria.
- The Ni content of forage crops, grown on soils with added Ni is also of particular concern from an animal health point of view because of the toxic nature of Ni to animals and humans
- The selection of species in such instances should be from plants of other families adapted to the particular climate and soil conditions which lead to the accumulation of only low amounts of Ni.
- *Ipomoea carnea, Datura stramonium and Calotropis gigantia* can be used for phytoremediation of Cd contaminated soils.

12. Future thrust

- A review of current research on rhizosphere –contamination interaction and its role in phytoremediation suggested that future research should be directed to establish the role of rhizosphere processes in the various phytoremediation technologies on specific metal basis.
- Advanced studies in Basic Research are required e.g. synchrotron-based XANES and XAFS spectroscopy for characterizing root exudates and metal-organic complexes in soil.
- Characterisation and quantification of rhizodeposites of fast growing trees by the synchrotron-based XANES spectroscopy coupled with mass spectrometric methods.
- Mechanism of metal-organic complexes in soil and its role in metal mobilisation in rhizosphere for developing a strategy for phytoremediation.
- Method for phytoremediation of metal-contaminated soil using fast growing trees
- Chemically enhanced phytoextraction and phytomining.
- Further research is needed in finding and cloning potentially useful genes, transforming and regenerating appropriate species, altering plant characteristic morphology, changing plant metabolism and adding degradative capacity to the rhizosphere.
- Database of soils with regards to background level, contamination levels and levels requiring intervention.
- Formulation of the guidelines for land application of solid and liquid wastes containing heavy metals based on systematic survey of waste disposal areas is required.
- Developments of infrastructure for waste water treatment.
- Farmers should be encouraged to grow non-edible but high value crops instead of vegetable crops.
- Implementation of laws that prohibit mixing of industrial effluents in sewage waters.
- Participatory Research Programme should be developed to bridge the gaps in knowledge and information.

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